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VOL. II

PRACTICAL CHEMISTRY

D.P. GOEL

PITAMBAR PUBLISHING COMPANY

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PRACTICAL CHEMISTRY

VOL. II

(FOR CLASS XII)

[Strictly according to the New Syllabus Prescribed by the Central Board of Secondary Education, New Delhi, in Practical Chemistry for Class XII]

2000

By

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PITAMBAR PUBLISHING COMPANY (P) Ltd.
Educational Publishers
888, East Park Road, Karol Bagh,
New Delhi-110 005 (INDIA)

Published by :
PITAMBAR PUBLISHING COMPANY Pvt. Ltd.
Educational Publishers
888, East Park Road,
Karol Bagh,
NEW DELHI-110 005 (INDIA)
Telephones : Off. : 770067, 776058, 526933
Res. : 5715182, 5721321, 586788

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ACC NO- 15195

First Edition : 1991

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Price : **Rs. 30·00**

Code No.* : *27713

Printed at :
SAINI PRINTERS
9/18, Bazar Gali,
Vishwas Nagar, Shahdara,
Delhi-110032
Phone : 2201564

Remembering
Matashri Late Smt. Satya Goel
who helped me in shaping my life.

Let us work as we pray; for indeed,
work is the body's best prayer to the Divine.

SYLLABUS IN CHEMISTRY PRACTICALS

CLASS XII

One Practical Paper   **Time : 3 hours**   **Marks : 30**

Core Experiments	**Marks**
(*i*) (*a*) Content Based Experiments	4
(*b*) Volumetric Analysis	6
(*c*) Mixture Analysis	10
(*ii*) Investigatory Project	5
(*iii*) Class Record and Viva	5

1. Preparation of double salt of ferrous ammonium sulphate or potash alum.

2. (*i*) Preparation of one lyophilic and one lyophobic sol.

Lyophilic sols—starch, egg, albumin and gum ;
Lyophobic sols—ferric hydroxide, aluminium hydroxide and arsenious sulphide.

(*ii*) Dialysis of sols prepared in 2 (*i*) above.

(*iii*) Comparison of the precipitation values of sodium chloride, barium chloride and aluminium chloride for arsenious sulphide sol.

3. Study of the role of emulsifying agents in stabilizing the emulsions of different oils.

4. Effect of concentration and temperature on the rate of reaction between sodium thiosulphate and hydrochloric acid.

5. (*i*) Separation of pigments present in leaves and flowers by paper chromatography. Determination of Rf values.

(*ii*) separation of constituents present in an inorganic mixture (constituents having wide difference in Rf values only will be provided).

6. Determination of the strength of $KMnO_4$ solution by titrating it against (*i*) oxalic acid solution, and (*ii*) ferrous ammonium sulphate solution.

7. **Qualitative analysis :**

Identification of two cations and two anions in a mixture :

Cations : Pb^{2+}, Cu^{2+}, Cd^{2+}, As^{3+}, Hg^{2+}, Al^{3+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+}, NH_4^+.

Anions : S^{2-}, SO_3^{2-}, SO_4^{2-}, CO_3^{2-}, NO_2^-, NO_3^-, Cl^-, Br^-, I^-, PO_4^{3-}, CH_3COO^-.

(N.B. : Insoluble salts and interfering ions are to be excluded. Also, two cations of the same group and anion combinations such as $(SO_4^{2-}+SO_3^{2-})$, $(NO_2^-+NO_3^-)$ or (Cl^-+Br^-) or (Br^-+I^-), $(CO_3^{2-}+C_2O_4^{2-}$ should be avoided).

8. Identification of cations and anions in common fertilizers.

9. Study of simple reactions of carbohydrates, fats and proteins in pure form and detection of their presence in given food stuff.

10. Test for the functional groups :

unsaturation, alcoholic group, phenolic group, aldehyde group, carboxylic group, ketonic group, amino group.

11. Distinguishing between following pairs of organic compounds by suitable chemical tests :

(*i*) Methanol and ethanol (*ii*) Benzaldehyde and acetone
(*iii*) Ethyl alcohol and phenol (*iv*) Phenol and benzoic acid
(*v*) Anilinc and phenol

12. Preparation of any two of the following :
(*i*) Iodoform, (*ii*) Aspirin, (*iii*) Acetanilide (*iv*) Di-benzal acetone (*v*) p—nitroacetanilide.

Suggestive Projects **Marks : 5**

[Any one is to be submitted at the time of final examination]

1. Study of diffusion of a solid into a liquid.
2. Determination of the minimum quantity of manganese dioxide required as a catalyst for the preparation of oxygen gas.
3. Determination of rate of flow of solutions and liquids horizontally.
4. Investigation on the foaming capacity of different washing soaps and the effect of addition of sodium carbonate on them.
5. Study of the acidity of different samples of the tea leaves and reasons for the variation in their taste.
6. Determination of the rate of evaporation of different liquids.
7. Study of the effect ofmetal coupling on the corrosion of iron.
8. Study of the effect of acids and bases on the tensile strength of fibres.
9. Analysis of fruit and vegetable juices for the contents (acids and minerals) present in them.
10. Preparation of rayon threads from various cellulose sources.
11. Study of dyeing of fabrics under various conditions.
12. Determination of the dosage of bleaching powder required for disinfection of different samples of water (taken from different sources).
13. Study of the presence of oxalate ions in guava fruit at different stages of ripening.
14. Study of the setting of mixtures of cement with lime, sand of different qualities, rice husk, etc. (with respect to time, volume and strength).
15. Study of the presence of insecticide/pesticide (nitrogen containing) in vegetables and fruits.
16. Study of the dialysis of different sewage water samples and identification of different ions in resulting solutions.
17. Study of quantity of casein present in different samples of milk.
18. Preparation of Soyabean milk and its comparison with the natural milk with respect to curd formation, effect of temperature, taste, etc.
19. Study of the effect of potassium bisulphate as food preservative under various conditions (temperature, concentration, time, etc.).
20. Study of digestion of starch by salivary amylase and effect of pH and temperature on it.
21. Comparative study of the rate of formation of following substances, wheat flour, gram flour, potato juice, carrot juice and organic juice.
22. Extraction of essential oils present in Saunf (Aniseed), Ajwain (Carum)] and Illachi (cardamom).
23. Study of constituents of an alloy (any sample easily available may be taken).
24. Study of common food adultrants in [fat, oil, butter, sugar, termuric powder, chille powder and pepper.

Note. Any other investigatory project can [be performed which involves about 10 periods of work with the approval of the teacher.

PREFACE

This laboratory manual is intended for class XII students. It meets the requirements of the syllabus prescribed by the Central Board of Secondary Education, New Delhi.

Each laboratory work is preceded by a brief theoretical introduction for independent study before the student proceeds to perform practical work in the laboratory. At the end of each unit, **oral questions with their answers**, have been included. It is an integral part of the laboratory work. Effort has been made to keep pace with the advances in laboratory work.

Care has been taken over the planning of each experiment so as to present the procedure, conclusion, etc. vividly. The subject matter and the experiments have been planned with a view to help the students of all levels.

In the last unit, a few investigatory projects have seen given within reasonable limits. The detailed investigations, observations and precise inference are left to the students. However, some sample observations and inferences are given.

The prime objective of introducing the investigatory project of the board has been to provide the students the taste of chemical research.

It is hoped that the book will meet the requirements of the students. We look forward to valuable suggestions from all our readers for further improvement of the book, as I earnestly believe in the following words from the Rigveda,

"Let noble thoughts come to us from every side".

Although considerable care has been taken in introducing the subject matter, yet the possibility of any error or ambiguity in matter/fact that may have found its way into the book in hand, cannot be ruled out.

I must thank Dr. Mohan Katyal, Dr. V.B. Agrawal, Dr. S.C. Vats, Shri R.S. Goel, Shri P.K. Gupta, Shri Surya Prasad, Shri Sumer Chand Bansal, Shri K.P. Sharma and Shri Pavan Chaudhary, for their constant encouragement in this humble endevour.

Finally, I must thank my wife Smt. Manju Goel and children Medha, Mayank and Manisha for their patience, help and cooperation at all times.

AUTHOR

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UNIT 1

Working in a Chemical Laboratory

1.1. INTRODUCTION

Chemistry laboratory is an integral part of a course of chemistry. It is necessary for the students to get familiarized with the equipments and permanent fixtures in the laboratory.

Work in a chemical laboratory is effective only when it is performed conscientiously, with an understanding of its theory and basic techniques. Moreover, every chemical operation requires that the experimenter be careful and attentive. Carelessness in handling the apparatus and lack of planning and organization of chemical work may result in serious consequences and incorrect results. This is why students are allowed to work in a laboratory only after preliminary briefing.

All laboratory works should be done by students individually. From the very first day in the laboratory, thought should be given to the time saving factor.

1.2. PROCEDURE OF WORK IN A LABORATORY

1. A student must read the description of the experiments he is to perform in the laboratory from standard texts, acquaint himself with the properties of the substances being studied, with the theory relating to the experiment and also note the special attention that the experiment demands.

2. Every student must keep his table clean and in good order. Only the objects needed for work must be on the table.

3. Every student should take the reagents in the quantities suggested. The stoppers of reagent bottles should be promptly replaced, and the bottles should be put back in their assigned place.

4. Take dry reagents or chemicals with a clean spatula or a small spoon. When taking solutions from reagent bottles, hold the atter with the labels upward (to prevent soiling them).

5. A reagent taken in excess (or unconsumed) should never be poured back into the bottle.

6. Never leave reagents taken from the shelves at your place of work.

7. Make use of the dropper for pouring solutions from bottles.

8. Use only distilled water when preparing aqueous solutions, washing precipitates, rinsing glass-ware and so on.

9. Always wear lab-coats when working.

10. Always follow the instructions sincerely given by your teachers.

Laboratory Notebook

A student working in a laboratory has to maintain a complete record of the experimental work done by him. The following points may be kept in mind for an ideal record of the practical notebook :

(*i*) All the pages of the record book should be numbered. Never remove any page from it.

(*ii*) Write the date and the object of the experiment at the top of the right hand page.

(*iii*) Enter your observations directly in the fair notebook. Never trust your memory in this respect, it often deceives you. It should never be written on the scraps of paper or filter paper.

(*iv*) Get your readings checked by the teacher before leaving the laboratory.

(*v*) Do not postpone the completion of your practical notebook till the next day. The work should be finished in the laboratory itself.

(*vi*) Mistakes should be crossed out with a single line. Do not erase anything in the notebook.

(*vii*) Write legibly and with good ink.

(*viii*) Always draw diagrams with pencil and on the left hand side of the record book.

(*ix*) Always write a new experiment on a fresh page. It gives a clear idea of the number of experiments done by you.

(*x*) The method employed in performing the experiment is to be written clearly and concisely. The conditions in performing the experiment should be specified. Changes taking place during the course of experiment should be recorded.

(*xi*) Get your record book signed by the teacher. Keep it clean and tidy.

An example for keeping an experiment record is given below :

Left hand page	**Right hand page**
Date............	Date............
(*i*) Experiment No.	(*i*) Experiment No.
(*ii*) Name of experiment	(*ii*) Name of experiment
(*iii*) Diagram with pencil	(*iii*) Apparatus and chemicals
(*iv*) Chemical equation (if any)	(*iv*) Theory
(*v*) Observations	(*v*) Procedure
(*vi*) Calculations	(*vi*) Precautions
Result	Result

Safety

Special precautions must be taken and safety rules observed in the laboratory.

Never work with highly inflammable substances near a lighted burner.

Keep working areas clear of books, *etc*.

Work far from a flame. Remember that clothes and hair will burn.

Point test tubes away from yourself and others.

Wear eyeshields if there is any risk to eyes.

Report any accident, however, small at once.

Don't taste anything. Find other ways to recognize substances.

Smell a gas with great care if necessary.

Beware of water when working with metallic sodium.

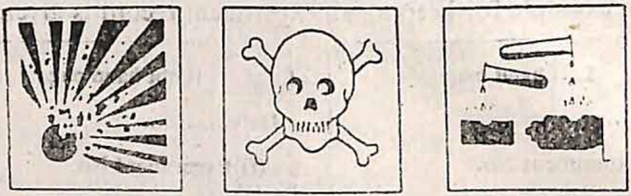
Never bend over a liquid being heated or substance being fused. to avoid splashes getting onto your face.

Perform all work with substances that are poisonous or have an unpleasant odour, and also the evaporation of acids and acidic solutions only in a fume-cupboard.

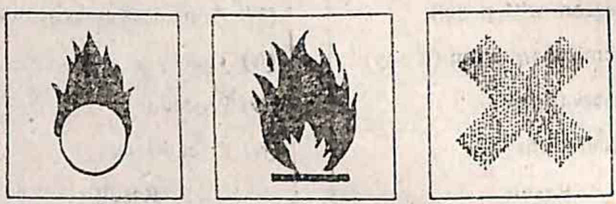
Never throw chemicals into the containers for waste.

Close the gas taps and water taps when not in use.

The drawings (Fig. 1.1) shown are labels. They are used for dangerous substances. Each picture explains what the danger is. They appear on bottles and containers.



EXPLOSIVE TOXIC (POISON) CORROSIVE



OXIDIZING AGENT (OXIDANT) FLAMMABLE (WILL BURN) HARMFUL OR IRRITATING

Fig. 1.1. Labels on bottles indicating what the danger is.

First Aid

1. If a concentrated acid (sulphuric, nitric, *etc.*) or an alkali solution gets on your skin (hands, *etc.*) immediately wash the burnt spot under running water for sufficient time. Now apply a cotton wool bandage soaked in an alcohol solution of tannin or a 3% potassium permanganate solution.

2. If splashes of an acid, ammonia, alkali, *etc.* get into your eyes, immediately wash them with plenty of water and consult a physician without delay.

3. If you have burnt your skin with a hot object, first apply a bandage soaked in an alcohol solution of tannin or a 3% potassium permanganate solution and then a bandage of ointment for burns.

4. If you have cuts with glass, *etc.*, first check for any glass piece and then apply a cotton wool bandage. If cuts are strong immediately see a physician.

5. If someone is poisoned by chlorine, hydrogen sulphide or carbon monoxide take him or her out into the open air and immediately call a physician.

6. If someone is poisoned by chemicals, take him or her immediately to a physician.

1.3. LABORATORY WARE

We are already familiar with the various types of glass-wares used in laboratory work. Common measuring vessels used in laboratory work are flasks, pipettes, burettes and measuring cylinders. A variety of heating equipments and heating aids is used in a laboratory, namely, gas burners, hot plates, baths, wire guaze, tripod stand, *etc*. There are some other aids which are found in the laboratory—iron stand, test tube stand, test tube brush, weight box, triangular file, cork, wash bottle, reagent bottle, chemicals, thermometer, filter paper, spatula, tongs, blow pipe, test tube clamp, *etc*.

Cleaning of Glass-wares

Cleanliness is very important. This attracts the students towards laboratory and fills them with zeal for working. Any trace of an impurity can affect the course of a chemical reaction. The apparatus should be thoroughly washed before starting as well as after finishing the experiment.

The glass apparatus is generally cleaned by scrubbing with washing soda (Na_2CO_3) or washing powder, such as Vim or Det. A suitable brush may be used for removing the dirt. It is then washed with tap water. Finally, it is rinsed with distilled water.

If the apparatus is very greasy or dirty, it should be treated with chromic acid (prepared by adding 5 g of commercially grade potassium dichromate to 100 ml of concentrated sulphuric acid with stirring and then cooling it). This ensures good wettability of the glass.

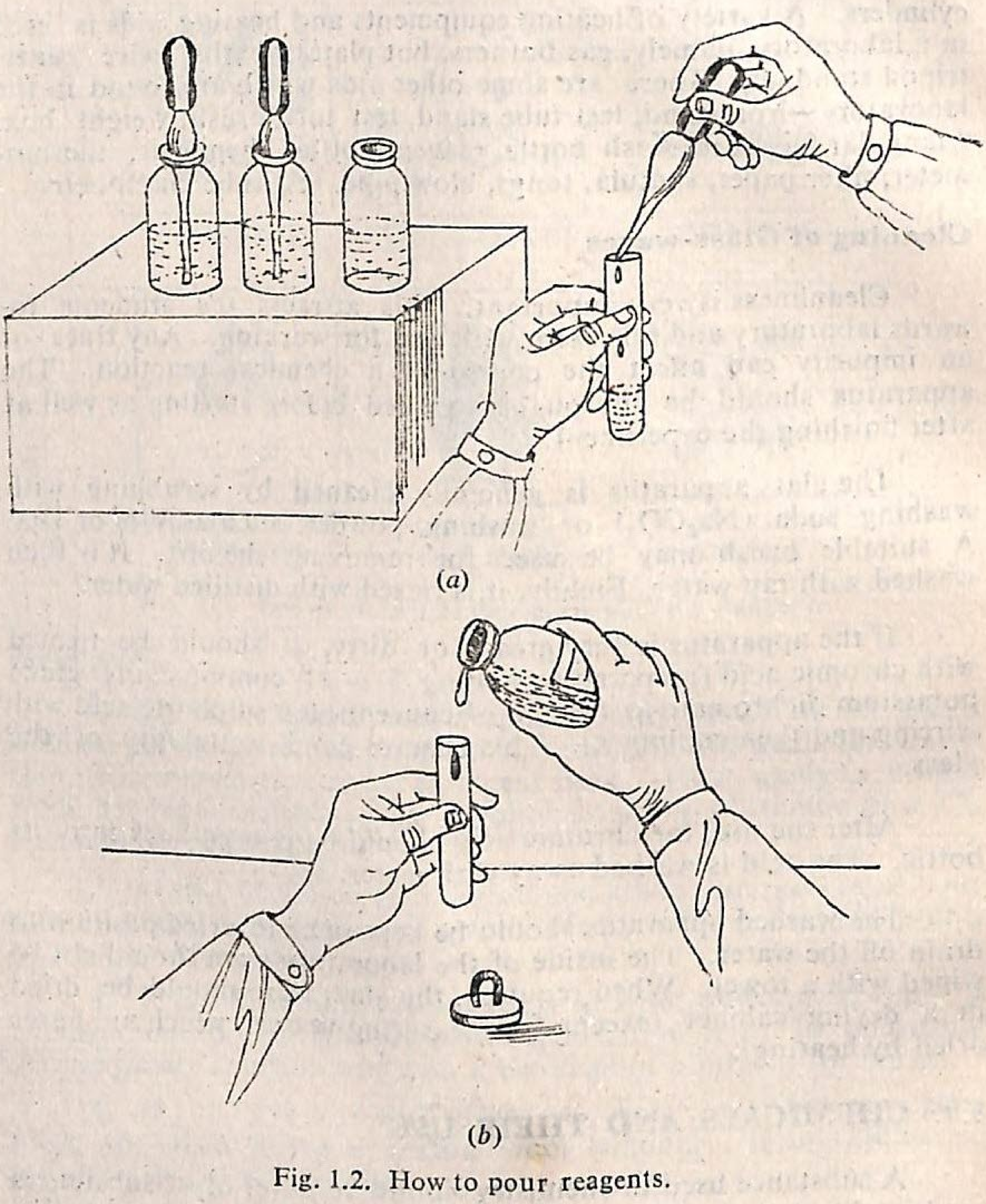
After the use, the chromic acid should be poured back into its bottle. The acid is washed away with water.

The washed apparatus should be kept in an inverted position to drain off the water. The inside of the laboratory ware should not be wiped with a towel. When required, the glass-ware should be dried in a drying cabinet (except for measuring vessels, which are never dried by heating).

1.4. CHEMICALS AND THEIR USE

A substance used in chemistry should be pure. Most substances used in chemistry are kept in glass or plastic bottles. Each has a label. It gives the chemical name of the substance and tells as how much pure it is.

The dry chemicals should be taken with a clean spatula or a special spoon. A dropper should be used for pouring liquids from bottles [Fig. 1.2(*a*)]. When pouring liquids from bottles [Fig. 1.2(*b*)] hold the latter with the labels upward (to prevent soiling them).



(a)

(b)

Fig. 1.2. How to pour reagents.

1.5. STUDY OF BURNERS

There are several types of Bunsen burners, but the working principle in each type is always the same. In a burner, oil or petrol gas is burnt in the presence of air to produce an intense and hot flame. The temperature of the flame can be controlled by regulating the flow of gas and air. The essential parts of a Bunsen burner (Fig. 1.3) are as follows :

(*i*) **Base.** It is a heavy metallic disc made of cast iron or brass. The base keeps the burner in a stable position. It is also provided with a side inlet tube for the gas. The inlet tube is connected by a rubber tubing to the gas tap.

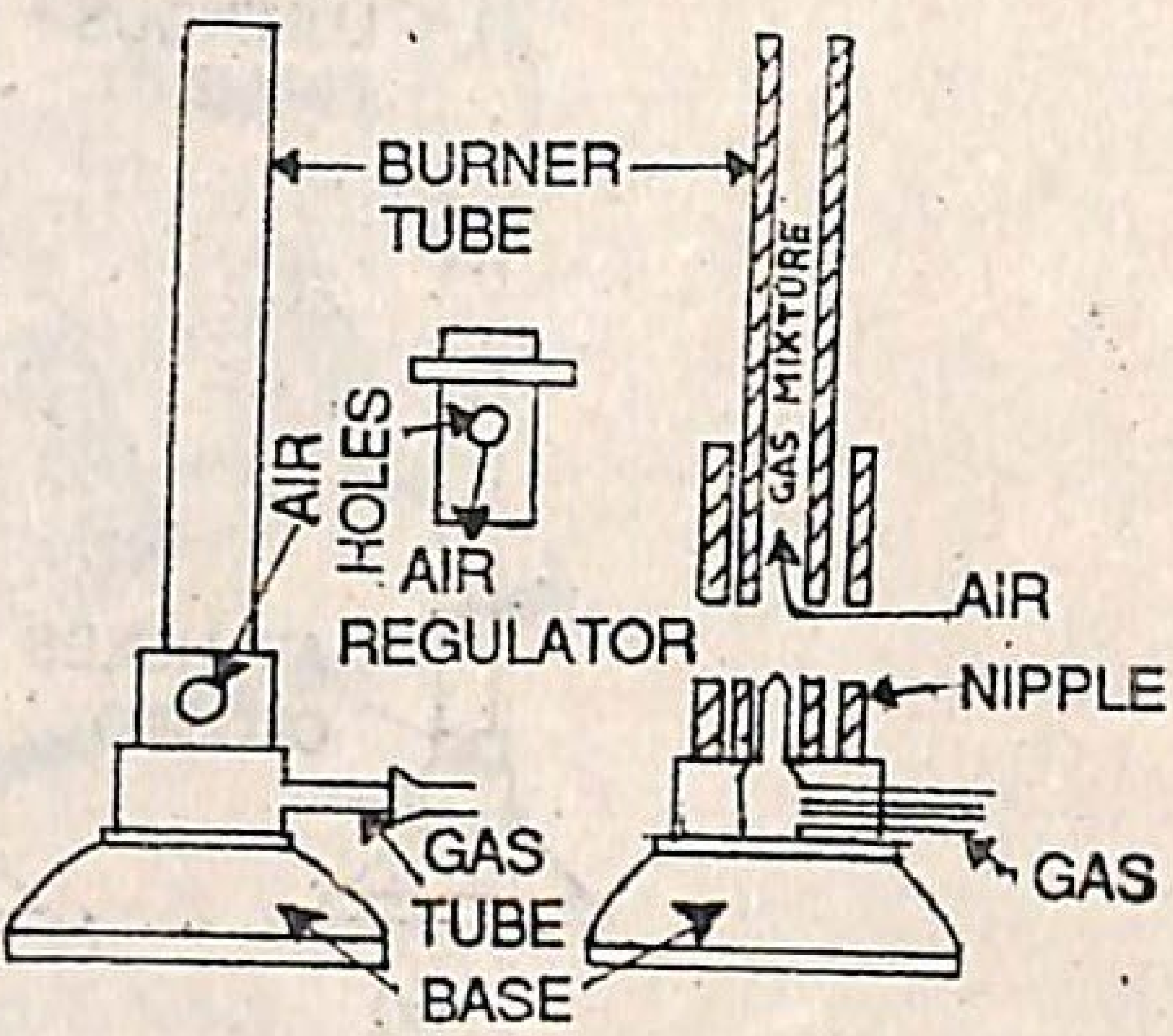


Fig. 1.3. Bunsen burner and its parts.

(*ii*) **Nipple**. It is generally made of brass. It is fitted just at the top of the base. It has a fine hole in the centre. The gas which enters the base through the side inlet comes out through the nipple under increased pressure into the burner tube.

(*iii*) **Burning Tube**. It is a long cylindrical tube about 10-15 cm in length. It is generally made of iron or brass. It has two holes opposite to each other above its lower end which serve as air holes. It can be screwed or unscrewed at the base. Gas and air enter this tube and burn at the top.

(*iv*) **Air Regulator**. It is a metallic ring which has two holes corresponding to the two air holes of the burner tube. It is provided at the lower end of the burner tube. By rotating the air regulator, it is possible to control the air holes thus regulating the supply of air.

Working. When the burner is to be used, the rubber tubing attached to its base is connected to the gas tap. The air regulator is adjusted to close the air holes. The gas tap is then opened and the lighted match is applied to the edge of the burner opening. The gas burns with a yellow flame, *i.e.*, it is luminous [Fig. 1.4 (*a*)]. This is caused by the reduced supply of air inside the tube. It is used only for reducing purposes and is, therefore, known as reducing flame.

When the air regulator is adjusted to open the air holes, the flame becomes non-smoky and non-luminous because of the complete combustion of the gas [Fig. 1.4 (*b*)]. This flame is used for general heating purposes. It has a higher temperature than the luminous flame. It is also known as an oxidizing flame.

Striking Back of the Burner. When the supply of the air in the gas-air mixture becomes high, the flame becomes unsteady and noisy. At times, the flame may even disappear and the gas burns at the mouth of the nipple, giving a small blue flame. This is known as the striking back of the flame. This makes the burner hot.

If the burner has struck back, close the gas tap, cool it, then light the burner again with a smaller opening for the air.

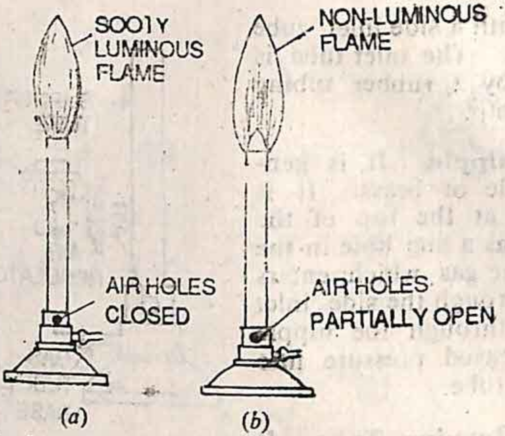


Fig. 1.4. Bunsen burner's flame when holes are (a) closed, and (b) opened.

It is possible to prevent the striking back of the burner by either decreasing the air supply or by increasing the gas supply.

Precautions. Whenever a burner is used in a laboratory, the following precautions should be kept in mind :

(*i*) Always keep the air inlets closed when lighting the burner.

(*ii*) To get a steady non-luminous flame, open the air holes gradually.

(*iii*) Regulate the flame by decreasing the supply of gas by adjusting the gas tap.

(*iv*) Always use the non-luminous flame for general heating purposes because it gives the maximum heat due to the complete combustion of the hydrocarbons.

(*v*) Do not throw any chemical into the flame. This enters the burner tube and block the nipple.

(*vi*) When the burner is not in use, put it off by closing the gas tap.

1.6. WEIGHING

Weighing with varied accuracy is required in laboratory work. For weighing, various types of balances have been designed: chemical balance, analytical balance, single pan balance, rough balance (Fig. 1.5), *etc.*

A conventional analytical balance can be used for weighing as much as 200 g with an accuracy up to 0.0002 g. It was invented by Lavoisier, the father of analytical chemistry. An analytical balance is shown in Fig. 1.6. The main parts of the balance are : the graduated metal beam, pillar, pointer, stirrups, pans, balancing or

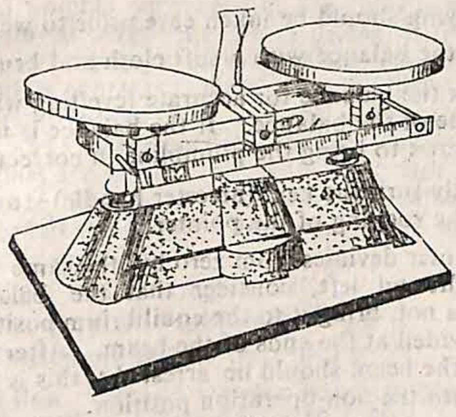


Fig. 1.5. Rough balance

levelling screw, index scale, knife edges, plumb line, key or lever, rider carrier.

The metal beam (equal-arm lever) is provided with three knife edges two at its ends and one in its middle. The middle knife edge rests on a place on the central pillar of the balance and provides support. The stirrups carrying the balance pans rest on the side knife edges. The beam is provided with a long pointer that points the deviation of the beam from a horizontal position (pointer is opposite zero) on a scale.

The balance is housed in a wooden cabinet whose front glass door can to raised and whose side glass doors can be opened. The cabinet protects the balance from dust and air streams. The latter make accurate weighing impossible.

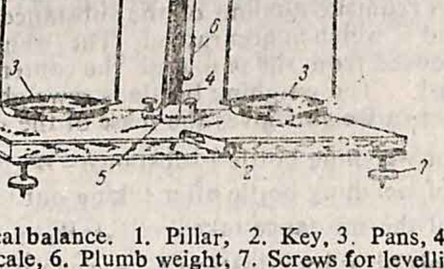


Fig. 1.6. Analytical balance. 1. Pillar, 2. Key, 3. Pans, 4. Pointer, 5. Graduated scale, 6. Plumb weight, 7. Screws for levelling the balance, 8. Beam, 9. Screws for balancing empty pans.

The following should be taken care prior to weighing :

(*i*) Clean the balance with a soft cloth and brush the pans.

(*ii*) Check the balance for accurate levelling which is indicated by the plumbline of the balance. If the balance is not in level, turn the levelling screws to bring the plumbline in correct position.

(*iii*) Gently turn the key (arrester handle) to the right (clockwise) and see the rocking of the pointer.

If the pointer deviates from zero by the same number of divisions to the right and left, consider that the balance is in a good order. If it does not, bring it to the equilibrium position by adjusting the screws provided at the ends of the beam. After the balance has been checked, the beam should be arrested ; this is done by moving the key back into the non-operation position.

Weighing Operation. Put the substance to be weighed on a dry glass plate or in a weighing bottle whose weight has been determined before hand. Place the object to be weighed on the left pan of the balance and the weights on the right pan. Turn the handle (or key) to the right and notice the movement of the pointer. If the pointer moves more towards the left, it indicates that the object is lighter than the weights in the right pan. This stage necessitates the removal of certain weights from the pan until the object is counterbalanced by the weights. However, if the pointer moves more towards the right, it indicates that the object is heavier and to counterbalance the object, addition of weights is required. Add or remove weights systematically to or from the right pan until the difference of the weights in the right pan and that of the object is less than 10 mg Now for final weighing, make use of the rider. When the pointer swings back and forth across the graduated scale an equal number of divisions on each side of the zero mark, the object is considered to show its correct mass. Now arrest the beam and record the weights placed in the right pan and the weight contributed by the rider (as calculated from its position).

Methods of Weighing

(*i*) **Weighing by difference**. A watch glass or weighing bottle is weighed. A requisite amount of the substance is taken in a weighing bottle and is weighed accurately. The weighing bottle is then carefully removed from the pan and the content is poured into the beaker or flask. The weighing bottle is reweighed with its remains. The difference in weights gives the mass of the substance taken.

Mass of weighing bottle+substance=W_1 g

Mass of weighing bottle after taking out the substance=W_2 g

Mass of the substance taken=(W_1-W_2) g

(*ii*) **Weighing by addition :** A clean watch glass is accurately weighed and a suitable amount of the substance is then added to it Required weights are placed on the right pan. The substance is added or removed from the watch glass a little at a time by a small spatula until the required weights are counterbalanced by the watch glass and its contents. Now when the balance is arrested, the watch glass is removed carefully and the substance is transferred to a beaker (or flask) and the particles of the substance still adhering to the watch glass are washed off with a stream of water from the wash bottle in the beaker. A substance can also be weighed in a weighing bottle but the addition and removal of substance becomes a time consuming exercise.

Accurate mass of watch glass$=W_1$ g
Mass of watch glass$+$substance$=W_2$ g
Mass of substance taken$=(W_2-W_1)$ g

Weight Box. This is a wooden box with grooves in which the nickel plated metallic weights of mass 50 g, 20 g, 20 g, 10 g, 5 g, 2 g, 2 g, and 1 g are kept (Fig. 1.7). There are fractional weights of mass 500 mg, 200 mg, 200 mg, 100 mg, 50 mg, 20 mg, 20 mg, 10 mg, 5 mg, 2 mg, 2 mg, and 1 mg. The fractional weights lower than 10 mg are generally not used. A rider is employed for weights lower than 10 mg.

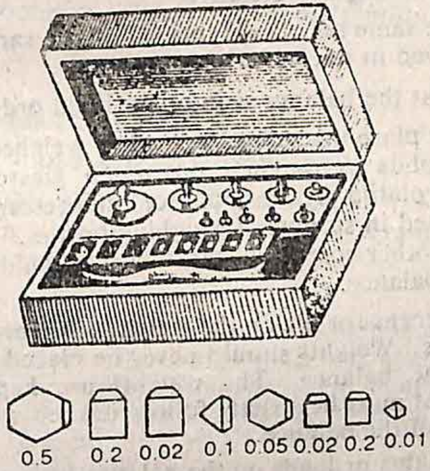


Fig. 1.7. Weight Box.

Rider. The rider is a curve shaped small piece of wire. It is made of aluminium, platinum or gold weighing 10 mg. When the rider is kept in the balance pan or it rests upon the tenth graduation mark of the beam which is vertically above the point of suspension of the pan, its full weight (10 mg) is taken into account. However, its effective weight in milligrams will vary according to the position of the rider on the graduated beam. The beam remains divided into 10 divisions on each side of the centre and the each division is further subdivided in five equal parts indicating 1/5th of a milligram. Divisions are always numbered. The rider on the beam is positioned with a rider carrier which can be moved to and fro. The effective-weight of the rider corresponds to the position in which it is placed.

Position of rider and its effective weight

Position on division	*Weight in gram*	*Position on Subdivision*	*Weight in gram*
1	0.001	1	0.0002
2	0.002	2	0.0004
3	0.003	3	0.0006
5	0.005	4	0.0008
7	0.007		

Precautions in using the balance

(*i*) Use the same set of weights and the same balance for all weighings involved in one experiment.

(*ii*) See that the balance is in operational order.

(*iii*) Never place the substances to be weighed directly on the balance pan. Solids are weighed on watch glasses or in weighing bottles whereas volatile, hygroscopic or efflorescent substances and liquids are weighed in stoppered weighing bottles. Caustic alkalis, liquid acids and other corrosive substances should not be weighed in an analytical balance.

(*iv*) Use forceps for lifting the weights. Never touch them with fingers and hands. Weights should never be placed on the table or on the floor of the balance. The weights are kept in a box in a definite order that must be strictly followed when weights are placed in the right pan of the balance.

(*v*) Put weights or loads on the balance pans and remove them only when the pans are arrested and the beam is raised.

(*vi*) Operate the key gently so as not to jerk the balance.

(*vii*) The substance and the weights should be placed on the pans and removed from them through the said doors. During weighing, and also when the balance is not being used, all the doors must be shut.

(*viii*) Do not weigh hot objects. Hot crucibles or some other objects, before weighing, be cooled in desiccators to room temperature.

(*ix*) After the weighing, the weights should be replaced in their respective nests in the box with the aid of forceps. The balance and the weights should always be left in order.

(x) Record the readings of weighings immediately in the practical record book.

1.7. PREPARATION OF SOLUTIONS

The concentration of solutions is, in most cases, expressed by the amount of the solute by mass in a definite mass or volume of the solution or the solvent. More specifically, concentration is usually expressed in one the following ways : as percentage concentration (%), as molar concentration (M), as molal concentration (m) or as normal concentration (N).

Molar Concentrations

The most useful way of expressing exact concentrations of solutions is in terms of moles of solute per litre of solution. Such concentrations are called molar and are designated by the letter 'M'. It expresses with considerable accuracy the exact number of particles (ions or molecules) per unit of solution volume.

$$\text{Molarity} = \text{moles of solnte per litre of solution}$$

$$= \frac{n}{V}$$

where n=number of moles

V=volume in litres of solution

A mole (6.02×10^{23} particles) of atoms or molecules is present in the atomic or molecular mass expressed in grams. This mass of any substance that contains a mole of particles is called the molar mass.

Thus, a mole of sodium atoms (atomic mass=23 amu) has mass of 23 g. Therefore, the molar mass of sodium is 23 g mol^{-1} (g mol^{-1} means g per mole). Similarly, a mole of water molecules (molecular mass=18 amu) has a mass of 18 g and thus the molar mass of water is 18 g mol^{-1}.

Now the molarity of a solution can be calculated from the expression,

$$\text{Molarity} = \frac{\text{Grams of a solute per litre}}{\text{Molar mass of the solute}}$$

While preparing the dilute solution of desired molarity and volume, we must be careful to distinguish between the concentration (molarity) and the amount (moles) of a solute in a solution. The concentration of a substance in a drop of its solution is the same as its concentration in a litre of the same solution. Obviously, the amount of the substance in its one litre solution is much greater than it is in the drop. If the drop were diluted to a litre of solution, the moles of solute would remain the same even though the concentration is greatly decreased.

∴ Number of moles before dilution = Number of moles after dilution

We know that number of moles = molarity × volume

$$n = M \times V$$

By substituting equals for equals, we get,

$$M_1V_1 = M_2V_2$$

where $$\frac{\text{mole}}{\text{L}} \times \text{L} = \frac{\text{mole}}{\text{L}} \times \text{L}$$

M_1V_1 = the number of moles before dilution

M_2V_2 = the number of moles after dilution

Normal Concentration

The normal concentration of a solution, designated by the letter '*N*' is another way of expressing the concentration of solutions. This method is based on the equivalent mass of the solute. A solution is said to be normal one, when it contains one gram equivalent of the solute per litre of the solution. The equivalent mass expressed in grams is called gram-equivalent. It is important to emphasize here that the gram-equivalent is not invariant as the gram-molecular mass is but depends upon the reaction concerned.

$$\text{Normality} = \frac{\text{Concentration in gram per litre}}{\text{Equivalent mass}}$$

Dilution problems involving normal concentrations are the same as with molar concentrations.

∴ Number of equivalents before dilution

= Number of equivalents after dilution

or

$$N_1V_1 = N_2V_2$$

$$\frac{eq}{\text{L}} \times \text{L} = \frac{eq}{\text{L}} \times \text{L}$$

As we known that the number of equivalents = NV, so it is simply a matter of substituting 'equals for equals'. Accordingly one mL of 1·0 N solution of any substance will react exactly with 1 mL of 1·0 N solution of another substance and that solutions of equal normality will react volume for volume.

Equivalent Mass

The definition of equivalent mass depends upon the type of reaction between the two reactants. The equivalent mass of a substance is that mass which in its reaction can correspond to 8.0 g oxygen or 1 g of hydrogen, or the equivalent. In the context of an acid an equivalent mass (simply called equivalent) of an acid is the mass of an acid that provides one mole of hydrogen ions. Thus,

H_3PO_4 contains three equivalents per mole, H_2SO_4 contains two equivalents per mole and HCl contains one equivalent per mole.

Examples

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + HOH(l)$$

$$H_2SO_4(aq) + 2NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2HOH(l)$$

$$H_3PO_4(aq) + 3NaOH(aq) \longrightarrow Na_3PO_4(aq) + 3HOH(l)$$

Similarly, an equivalent of a base is the mass required to supply one mole of hydroxide ions in a reaction. Thus, in order to find out the equivalent mass of an acid, it is important to know how many protons of an acid could be replaced by a base. Equivalent mass of an acid is thus defined as that mass of the acid which contains one replaceable hydrogen atom, *i.e.*,

$$\text{Equivalent mass of acid} = \frac{\text{Molecular mass of acid}}{\text{Number of replaceable H atoms}}$$

$$= \frac{\text{Molecular mass}}{\text{Basicity}}$$

Similarily, the equivalent mass of a base is the mass of the base which contains one replaceble hydroxyl group, *i.e.*,

$$\text{Equivalent mass of base} = \frac{\text{Molecular mass of base}}{\text{Number of } H^+ \text{ ions which react with a molecule of base}}$$

$$= \frac{\text{Molecular mass}}{\text{Acidity}}$$

The equivalent mass of a salt is generally calculated by dividing the molar mass by the total positive (or negative) valence. Examples of equivalent of some acids, bases, and salts are tabulated below :

Equivalent masses of some important acids

Name of acid	*Formula of acid*	*Molecular mass (M)* *Molar mass* (g/mol)	*No. of replaceable H atoms (B)*	*Equivalent mass* (g/equiv.) (M/B)
Hydrochloric acid	HCl	36.5	1	36.5
Sulphuric acid	H_2SO_4	98	2	49
Nitric acid	HNO_3	63	1	63
Oxalic acid	$\begin{array}{l}COOH\\ \vert\\ COOH\end{array} 2H_2O$	126	2	63
Acetic acid	CH_3COOH	60	1	60
Phosphoric acid	H_3PO_4	98	3	32.7

Equivalent masses of some important bases and salts which behave like bases.

Name of base	*Formula of base*	*Molecular mass (M)* *Molar mass* (g/mol)	*Acidity (A)*	*Equivalent mass* (g/equiv.) (*M*/*A*)
Sodium hydroxide	$NaOH$	40	1	40
Potassium hydroxide	KOH	56	1	56
Calcium hydroxide	$Ca(OH)_2$	74	2	37
Sodium carbonate	Na_2CO_3	106	2	53
Potassium carbonate	K_2CO_3	138	2	69
Sodium bicarbonate	$NaHCO_3$	84	1	84
Potassium bicarbonate	$KHCO_3$	100	1	100

Equivalent masses of some important salts

Compound	*Molar mass* (g/mol)	*Total positive volume*	*Equivalent mass* (g/equiv.)
KCl	74.5	1	$74.5 \div 1 = 74.5$
$NaCl$	58.5	1	$58.5 \div 1 = 58.5$
Na_2SO_4	142	2	$142 \div 2 = 71$
$AlCl_3$	133.5	3	$133.5 \div 3 = 44.5$
$Al_2(SO_4)_3$	342	6	$342 \div 6 = 57$

The equivalent mass of a substance involved in oxidation-reduction titrations is defined as the mass of the substance which consumes or produces 1 mole of electrons directly or indirectly. Numerically, this may be expressed as follows :

$$\text{Equivalent mass} = \frac{\text{Molecular (or ionic) mass}}{\text{Number of electrons gained or lost per molecule (or ion) of the substance}}$$

From the above definition it follows that the determination of the equivalent mass of an oxidizing or reducing agent involves the following steps :

(*i*) Complete and balanced ionic equation for its reduction or oxidation reaction, and

(*ii*) The number of electrons required or lost per molecule as per the balanced ionic equation. The balanced ionic equation of $KMnO_4$ in acid solntion is

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

From this equation it is evident that five electrons are gained by each MnO_4^- during the course of the reaction.

Therefore,

$$\text{Equivaleat mass of } MnO_4^- = \frac{\text{Ionic mass of } MnO_4^- \text{ ion}}{5}$$

The following table gives the equivalent masses of commonly used substances in redox titrations.

Name of the substance	*Molecular formula*	*Molecular mass*	*Ion-electron equation*	*Number of electrons gained or lost per molecule* (n)	*Equivalent mass* (M/n)
Potassium permanganate	$KMnO_4$	158	$MnO_4^- + 8H^+ + 5e^-$ $\rightarrow Mn^{2+} + 4H_2O$	5	$\frac{158}{5} = 31.6$
Ferrous sulphate	$FeSO_4.7H_2O$	278	$Fe^{2+} \rightarrow Fe^{3+} + 1e^-$	1	$\frac{278}{1} = 278$
Mohr's salt	$FeSO_4.(NH_4)_2SO_4.6H_2O$	392	$Fe^{2+} \rightarrow Fe^{2+} + 1e^-$	1	$\frac{392}{1} = 392$
Oxalic acid	$\begin{array}{l} COOH \\ \vert \\ COOH \end{array} 2H_2O$	126	$\begin{array}{l} COO^- \\ \vert \\ COO^- \end{array} \rightarrow 2CO_2 + 2e^-$	2	$\frac{126}{2} = 63$
Potassium dichromate	$K_2Cr_2O_7$	294	$Cr_2O_7^{2-} + 14H^+ + 6e^-$ $\longrightarrow 2Cr^{3+} + 7H_2O$	6	$\frac{294}{6} = 49$

$$\text{Equivalent mass of } KMnO_4 = \frac{\text{Molecular mass of } KMnO_4}{5}$$

$$= \frac{158}{5} = 31.6$$

Standard Solutions

A solution of known concentration is considered as a standard solution. The strength of a standard solution is expressed in gram equivalents per litre or moles per litre. For example, if 8 g of a substance is dissolved in one litre solution, its strength is 8 g/L.

Some of the standard solutions are prepared by weighing out accurately and dissolving the weighed solute in a suitable solvent and making up the solution to a known volume. Standard solutions of sodium carbonate, oxalic acid, potassium dichromate, *etc*. are prepared in this way. These substances are available in the pure form (analytical grade) and are called **primary standard substances**. Their solutions of known concentration are called primary standard solutions as other solutions are standardized against them.

A primary standard substance must have the following characteristics :

(*i*) It should be easily available in the pure state.

(*ii*) It should be stable at room temperature.

(*iii*) Its composition should not change when stored.

(*iv*) It should be readily soluble in water.

Crystalline oxalic acid, sodium carbonate Mohr's salt, *etc*. have all the characteristics of primary standard substances.

Substances which do not meet the above requirements are called **secondary standard substances**. Standard solutions of these substances cannot be prepared by dissolving their known amount in a solvent. For the preparation of standard solutions of such substances, as HCl, H_2SO_4, $KMnO_4$, NaOH, aqueous ammonia, *etc*., first solutions of approximate concentration are prepared and then standardized by titrating against a suitable primary standard solution. Concentrated HCl is about 12N and the strength of conc H_2SO_4 is about 36N. Hence, the solutions of these acids of approximate strength are prepared by diluting their calculated volume to a known volume.

1.7.1. Preparation of the Standard Solution

(*i*) Take a clean and dry weighing bottle. Weigh the weighing bottle accurately and record its mass in your record book.

(*ii*) Put the substance with a spatula in the weighing bottle and take its mass again. The difference between the initial mass of the weighing bottle and that of weighing bottle with its contents should correspond to the calculated amount of the substance. Again record its mass in your record book.

(*iii*) Transfer the weighed substance from the weighing bottle to a 250 mL beaker (Fig. 1.8). If the substance is weighed by difference method, the weighing bottle should now be weighed again. If not, the weighing bottle should be washed with its contents. Transfer these washings to the beaker.

(*iv*) Add distilled water from a wash bottle along the sides of the beaker so that there is no splashing.

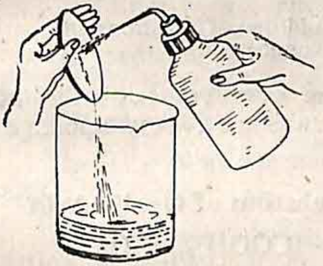


Fig. 1.8. Transferring of a weighed substance to a breaker for dissolution.

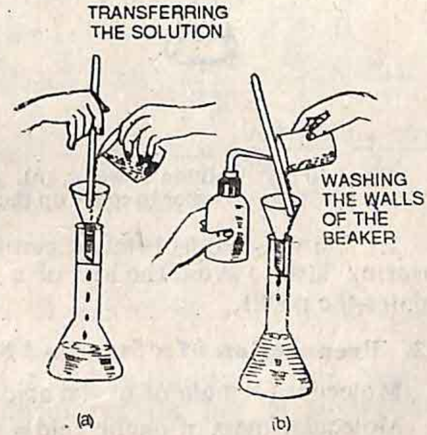

TRANSFERRING THE SOLUTION
WASHING THE WALLS OF THE BEAKER
(a)
(b)

Fig. 1.9 (*a*) Transferring the solution into a measuring flask, (*b*) Washing the inner surface of the breaker and transferring the washings into the flask.

(*v*) Dissolve the substance by stirring it gently with a glass rod.

(*iv*) After ensuring the complete dissolution of the substance transfer the entire solution into a measuring flask with the help of a funnel [Fig. 1.9 (*a*)].

(*vii*) Wash the entire interior surface of the breaker with distilled water and transfer the washings into the measuring flask [Fig. 1.9 (*b*)].

(*viii*) Now add more of distilled water from a wash bottle taking care not to fill upto the mark but a little below it [Fig. 1.10(*a*)]. Finally add a few drops of distilled water with a pipette until the lower level of the meniscus just coincides the graduated mark on the flask [Fig. 1.10 (*b*)].

(*ix*) The measuring flask is then stoppered and shaken vigorously for a few minutes to make the solution homogenous.

Note. 1. The substance can be weighed in a watch glass also.

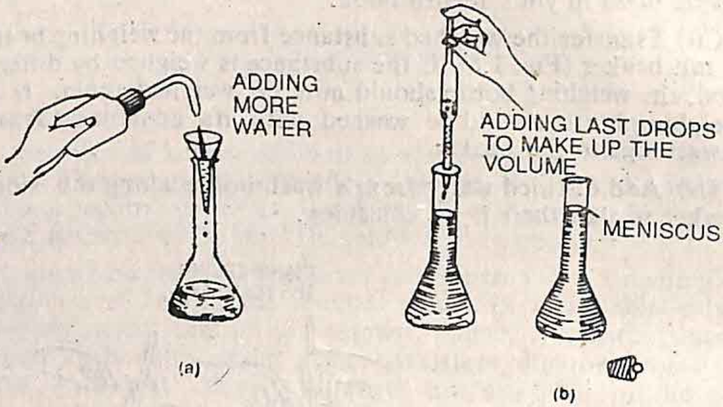


Fig. 1.10 (*a*) Addition of water, (*b*), Addition of last drops of water to make up the volume.

2. The weighed substance can be transferred directly into a measuring flask to avoid the loss of a substance. Any spoilage invalidates the result.

1·7·2. Preparation of a Standard Solution of Oxalic Acid

Molecuar formula of oxalic acid$=(COOH)_2.2H_2O$

Molecular mass of oxalic acid$=126$ g

To prepare 1000 mL of 1M oxalic acid, 126 g of oxalic acid is required. To prepare 1000mL of $\frac{M}{15}$ oxalic acid $\frac{126}{10}$ g or 12.6 g of oxalic acid is required. And to prepare 250 mL of $\frac{M}{10}$ oxalic acid $\frac{12.6\times250}{1000}$ g or 3.15 g of oxalic acid is required.

Now to prepare a normal solution, equivalent mass of oxalic acid is required. Its equivalent mass is half of its molecular mass as the oxidation of one molecule of oxalic acid liberates two electrons or it contains two replaceable hydrogen atoms. Now to prepare 250 mL of $\frac{N}{10}$ oxalic acid, $\frac{63\times250}{1000}$ g or 1.575 g of oxalic is required.

In general,

$$\text{Normality}=\frac{\text{Mass of substance}}{\text{Equivalent mass}}\times\frac{1000}{\text{Volume of solution}}$$

$$\text{Normality}=\frac{1}{10}$$

Mass of substance required $= x$ g

Equivalent mass $= 63$

Volume of solution required $= 250$ mL

$$\frac{1}{10} = \frac{x}{63} \times \frac{1000}{250}$$

$$x = \frac{1}{10} \times \frac{63 \times 250}{1000} = 1.575 \text{ g}$$

Now weigh the calculated amount of oxalic acid as suggested in Sections 1.6 and 1.7.1. Dissolve the sample as suggested.

Mass of watch glass $= w_1$ g

Mass of watch glass + oxalic acid $= w_2$ g

Mass of oxalic acid $= (w_2 - w_1)$ g

Volume of solution to be prepared $= 250$ mL

$$\text{Normality of oxalic acid} = \frac{w_2 - w_1}{63} \times \frac{1000}{250} = \frac{4(w_2 - w_1)}{63}$$

$$\text{Molarity of oxalic acid} = \frac{w_2 - w_1}{63} \times \frac{1000}{250} = \frac{4(w_2 - w_1)}{126}$$

The terms 'mass' and 'weight' are loosely equated in practice.

1.7.3. Preparation of a Standard Solution of Sodium Carbonate

The molecular formula of anhydrous sodium carbonate is Na_2CO_3.

The equivalent mass of a salt taking part in an acid-alkali titration is calculated by making use of the law of equivalents or using is formula,

$$\text{Equivalent mass of } Na_2CO_3 = \frac{\text{Molecular mass}}{\text{Acidity}}$$

$$= \frac{106}{2} = 53$$

Thus to prepare 1000 mL of I N sodium carbonate solution 53 g of salt is required.

To prepare 1000 mL of N/10 sodium carbonate solution, 53/10 g or to prepare 250 mL of N/10 sodium carbonate solution $\frac{53 \times 250}{1000}$ g or 1.325 g of sodium carbonate is required.

Weigh 1.325 g of sodium carbonate in a watch glass and dissolve the sample as suggested in Sec. 1·7·1.

Mass of watch glass $= w_1$ g

Mass of watch glass + sodium carbonate $= w_2$ g

Mass of sodium carbonate $= (w_2 - w_1)$ g

Volume of solution to be prepared $= 250$ mL

15195

Normality of sodium carbonate

$$=\frac{\text{Mass of sodium carbonate}}{\text{Equivalent mass}}\times\frac{100}{\text{Volume of solution}}$$

$$=\frac{(w_2-w_1)}{53}\times\frac{1000}{250}$$

$$\text{Normality}=\frac{4(w_2-w_1)}{53}$$

Molecular mass of sodium carbonate=106

$$\text{Molarity of sodium carbonate}=\frac{4(w_2-w_1)}{106}$$

1.7.4. Standard Solutions of Acids

The most commonly used acid solutions in the laboratory are hydrochloric, sulphuric, nitric and acetic acids. These acids cannot be weighed like crystalline substances for preparing their solutions of known concentrations. Therefore, it is important to know the methods by which their standard solutions can be prepared. The concentrations of these commonly used acids are as follows :

Acid	*Specific gravity*	*Approximate normality*
Hydrochloric acid	1.19	12 N
Nitric acid	1.42	16 N
Sulphuric acid	1.84	36 N
Acetic acid	1.05	14 N

For preparing dilute solutions of acids of required concentrations of acids, we can use the normality equation to calculate the volume of a given acid to be taken.

$$N_1V_1=N_2V_2$$

For example, if we have to prepare 250 mL of 5N sulphuric acid from 36 N concentrated acid, the volume of concentrated sulphuric acid required will be about 35 mL, *i.e.*,

$$36\text{ N}\times V_1=5\text{N}\times 250$$

or

$$V_1=\frac{5\times 250}{36}=\frac{1250\text{ mL}}{36}\cong 35\text{ mL}$$

Thus, 35 mL of concentrated sulphuric acid is taken and diluted to 250 mL in a measuring flask. **The acid should be poured into water and not water into the acid.** This acid solution will be about 5N because the acid available in the market may not be exactly 36 N.

For preparing 250 mL of N/10 sulphuric acid, the concentrated acid required will be about 0.7 mL, *i.e.*,

$$36\ N\times V_1=\frac{N}{10}\times 250$$

or

$$V_1=\frac{25}{36}\cong 0.7\ \text{mL}$$

1.7.5. Preparation of Dilute Solutions (known Concentrations) of Sulphuric acid

(*i*) To prepare 250 mL 1 N H_2SO_4 take 7 mL pure conc. H_2SO_4 with the help of a measuring cylinder (10 mL capacity) and pour it slowly into the 500 mL beaker containing about 200 mL distilled water. Stir the solution by a glass rod. After all the acid has been added allow the solution to stand at room temperature. Now transfer the solution into a 250 mL measuring flask with the help of a funnel. Add more of distilled water upto the mark. After stoppering the measuring flask, shake the solution thoroughly for 2-3 min to make the solution homogeneous. The solution will be about 1N.

The solution of H_2SO_4 can be standardized by titrating against standard sodium carbonate solution. The detailed procedure for standardizing the solution is given in Unit 7.

(*ii*) To prepare 250 mL 0.1 N H_2SO_4 0.7 mL pure conc. H_2SO_4 with the help of a measuring cylinder (1.0 mL or 10 mL capacity). Now follow the procedure as given above. Label the resulting solution as 0.1 N H_2SO_4.

Remarks. (*i*) When ~ 22.5 mL of conc. hydrochloric acid is made upto 250 mL with distilled water, the dilute solution so prepared would approximately be of strength 1 N (or 1M).

(*ii*) When ~ 16 mL of conc. nitric acid is made upto 250 mL with distilled water, the dilute solution of the acid so prepared would approximately be of strength 1 N (or 1 M).

(*iii*) When ~ 7.0 mL of conc. H_2SO_4 is made upto 250 mL with distilled water, the dilute solution of the acid so prepared would approximately be of strength 1N (or 0.5 M because basicity of H_2SO_4 is 2).

Precautions. 1. Acids being highly corrosive, should be handled with extreme care.

2. Aprons should be used to protect clothes.

3. While preparing dilute solutions of acids, acids should be pour into water. Special care should be taken in the case of sulphuric acid.

The following tables include the details about the common concentrated acids and outlines for preparing dilute acids from them.

Concentrated acids

Acid	*Percent by mass*	*Approximate specific gravity*	*Normally*	*Volume required to make 1 litre of approximately 1* N *solution* (mL)	*Volume required to make 250* mL *of approximately* N/10 *solution* (mL)
Hydrochloric acid (HCl)	35	1.18	12 N	90	2.2
Nitric acid (HNO_3)	70	1.42	16 N	65	1.6
Sulphuric acid (H_2SO_4)	98	1.84	36 N	30	0.7
Acetic acid (CO_3COOH)	99.6	1.05	16 N	60	1.5

Diluted Acids

Acid	*Approximate normality*	*Preparation*
Hydrochloric acid (HCl)	4 N	Dilute 334 mL of conc. HCl to 1 litre with distilled water.
Nitric acid (HNO_3)	4 N	Dilute 248 mL of conc. HNO_3 to 1 litre with distilled water.
Sulphuric acid (H_2SO_4)	4 N (2 M)	Add 112 mL of conc. H_2SO_4 slowly and with constant stirring into about 500 mL of distilled water. Cool it and make upto a litre by distilled water.
Acetic acid	4 N	Dilute 255 mL of glacial acetic acid to 1 litre with distilled water.

Note: For diluting sulphuric acid solutions, the acid is added into water. Water is never added to the sulphuric acid solution.

1.7.6. Preparation of Dilute Solutions (Known Concentrations) of Bases

The most commonly used base solutions in the laboratory are sodium hydroxide and aqueous ammonia. Sodium hydroxide is a deliquescent solid; its standard solutions cannot therefore be prepared by direct weighing. It is usual to prepare a solution of approximately the concentration required and then to standardize it against standard oxalic acid solution (Unit 7).

Ammonium hydroxide in solution is only slightly split up into ammonium and hydroxide ions. Because of this, at times, it is called aqueous ammonia. On standing, dissolved ammonia gas evaporates. Its strength decreases with lapse of time. It is usual to prepare its standard solution as and when required. A solution of ammonium hydroxide smells of ammonia. This is because the reaction of ammonia with water is reversible.

$$NH_4OH(aq) \rightleftharpoons NH_3(g) + H_2O(l)$$

The decomposition is accelerated by heat and also by blowing air through the solution.

The following table includes the details about the solutions of ammonia and sodium hydroxide and their method of preparation.

Solutions of ammonia and sodium hydroxide

Name	*Molecular formula*	*Approximate normality*	*Preparation*
Conc. ammonia solution	NH_3	15 N	Prepared by diluting the liquefied ammonia. It contains approximately 28% of ammonia by mass. Its specific gravity is @ 0.88.
Dilute ammonia solution	NH_4OH	4 N	Dilute 268 mL of the conc. ammonia to one litre by distilled water.
Sodium hydroxide solution	NaOH	4 N	Dissolve 176 g sodium hydroxide pellets in distilled water. Cool it and dilute to make the solution one litre.

1.7.7. Preparation of Solutions to be used as Laboratory Reagents

In the laboratory, reagent solutions of definite concentrations are used. Chemically pure compounds are dissolved in distilled water or some other solvent to prepare their solutions.

If a substance is water soluble, but turbidity or a precipitate appears in its aqueous solution on standing as a result of hydrolysis of the dissolved substance, the appropriate acid is added to the solution (HCl to chlorides, HNO_3 to nitrates, and so forth). Some reagents, especially organic ones are not water-soluble, and therefore, organic solvents (alcohol, acetone, and so forth) are used for dissolving them.

For the preparation of acid and base solutions (laboratory reagents), the procedure has already been suggested. For preparing some other individual reagent solutions, the procedures have been given in Appendix.

□ □

UNIT 2

Preparation of Crystals

2.1. INTRODUCTION

A substance used in chemistry should be pure. If not, we get wrong ideas about it. In daily life, 'pure' has a different meaning. We buy pure honey. We eat pure butter. We wear clothes made of pure wool. Honey, butter and wool are mixtures. In science 'pure' has only one meaning. A pure substance is a single substance. Definite physical and chemical properties and colour and shape of the crystals of a substance are attributed to its purity.

Chemical substances can be recognized by the shape of their crystals and their colours. A substance (element or compound) acquires a definite crystalline shape depending on the conditions under which it crystallizes out from its solution. Growing crystals provide a pleasing experience and wonderful sight to chemists. The crystals, if grown under suitable conditions, will appear in their desired forms. However, some crystals are easier to grow than others, *e.g.*, large crystals of common salt and washing soda are difficult to obtain while those of alums are easier to grow.

2.2. FORMATION OF CRYSTALS

One should bear in mind the following points while growing crystals from their solutions :

(*i*) Crystals can only be obtained from a saturated solution of a substance because a cold solvent is unable to hold as much solute as a hot solvent.

(*ii*) Inorganic substances are highly soluble in hot water.

(*iii*) For the proper growth of crystals, at times, a bit of crystal called 'nucleus' is required, around which the crystal can grow. It may also result from the molecules present in solution coming closer by chance. More often it is provided by some particle of dust, caught by the solution as per chance only. A dirty solution can provide a larger number of nuclei, thus resulting into the growth of many small crystals. Therefore, the solution should always be filtered and protected from dust particles before keeping for crystallization.

(*iv*) Evaporation or quick cooling of hot saturated solution should be avoided. As a result, the excess solute is deposited from the solution, and the deposit is obtained as crystals. Thus, rapid cooling will give small crystals.

Slow cooling of the hot saturated solution (gradual crystallization) will give fewer but large crystals. Thus on evaporation or cooling crystals form. This is because the particles collide and then stay together.

(*v*) During the course of crystallization, the solution should not be disturbed. The size and shape of crystals may change on disturbing the solution.

The process of crystal formation involves the following steps :

1. **Preparation of saturated solution of a substance.** A saturated solution is defined as one that contains the maximum amount of solute at a given temperature. Thus, a saturated solution is prepared by taking a required amount of the substance in a beaker and adding water just sufficient to dissolve the substance. At times, a saturation stage is reached by concentrating the solution.

2. **Filtration.** The saturated solution is filtered hot in a china dish to remove any suspending impurities.

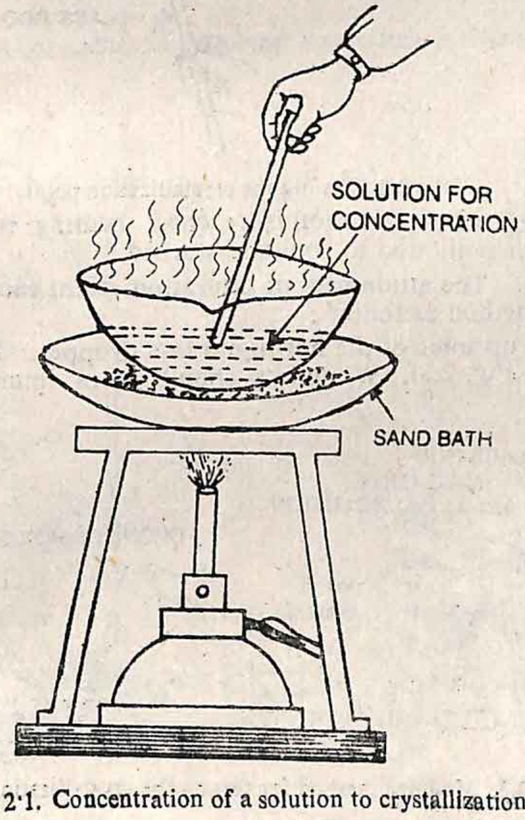


Fig. 2·1. Concentration of a solution to crystallization.

3. **Crystallization.** The filtrate of hot saturated solution is cooled slowly to initiate the process of gradual crystallization.

For a better yield, gentle heating of the solution is required on a sand bath. The solution is concentrated to a saturation point (Fig. 2.1). To test the stage of saturation point, air is blown from mouth on a glass rod dipped into solution (Fig. 2.2). If a deposit appears on the glass rod, the heating of the solution is suspended. The deposit ensures the crystallization point.

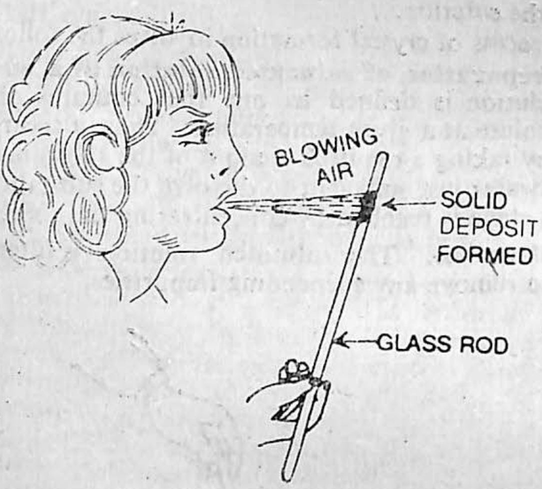


Fig. 2.2. Testing the crystallization point.

After the crystallization is reached, heating is suspended and the solution is allowed to cool undisturbed.

Note. The attainment of saturation point can be tested by a modified method as follow :

Take up some of the hot liquid in a dropper. Put drops on a glass slide (Fig. 2.3). White bits should form immediately in the drops.

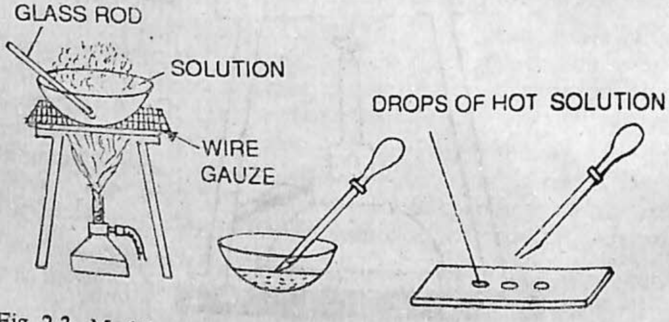


Fig. 2.3. Modified method for testing the crystallization point.

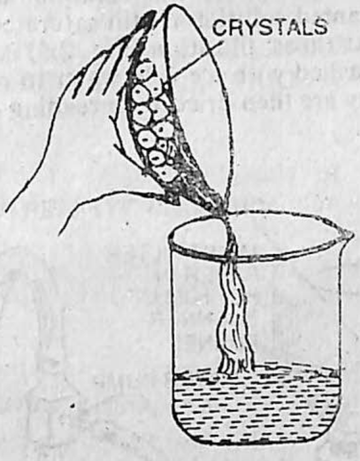


Fig. 2.4. Decanting off the mother liquor from the crystals.

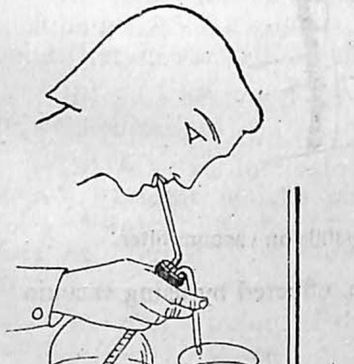


Fig. 2.5. Filtration of the crystals and their washing with ice cold water.

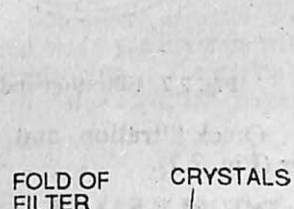


Fig. 2.6. Drying of the crystals,

4. **Filtration and drying of crystals**. When the process of crystallization is complete, the solution left is decanted off (Fig. 2.4). The decanted solution is still saturated and is called the **mother liquor**. At times, filtration (Fig. 2.5) is also required. The crystals are then washed with ice-cold water to remove the adhering mother liquor. They are then dried by spreading over a layer of filter paper (Fig. 2.6).

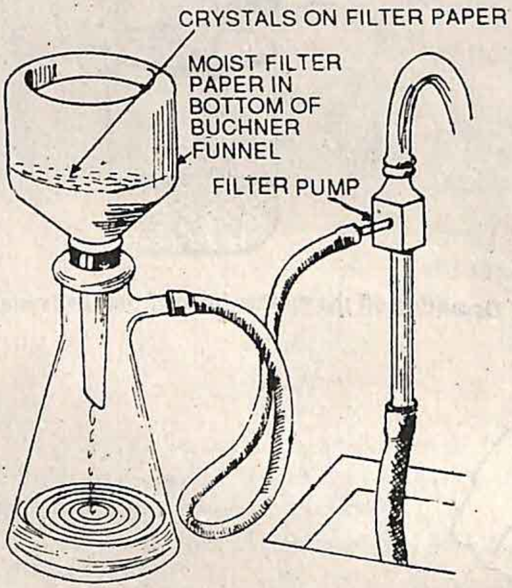


Fig. 2.7. Filtration and drying of the crystals on vacuum filter.

Quick filtration and drying can be effected by using vaccum filter (Fig. 2.7).

2.3. DOUBLE SALTS

A compound of two normal salts which forms crystals, *e.g.* aluminium potassium sulphate.

A special series of double salts is called 'Alums'. Their general formula is

$$\overset{I}{M}_2SO_4.\overset{III}{M}_2(SO_4)_3\ 24H_2O$$

where $\overset{I}{M}=Na^+, K^+, Rb^+, Cs^+, NH_4^+, Tl^+$ or Ag^+

and $\overset{III}{M}=Al^{3+}, Fe^{3+}, Cr^{3+}$, *etc.*

Thus, alums are hydrated sulphates containing both uni- and tripositive ions. Some of the well known alums are :

Potash alum	$K_2SO_4.Al_2(SO_4)_3.24H_2O$
Ferric alum	$(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$
Chrome alum	$K_2SO_4.Cr_2(SO_4)_3.24H_2O$.

2.4. EXPERIMENTS

Experiment 2·1. To prepare crystals of copper sulphate ($CuSO_4.5H_2O$) by reacting cupric oxide with concentrated sulphuric acid.

Apparatus. Beakers, funnel, glass rod, filter paper, evaporating dish, funnel stand, tripod stand, wire guaze, burner, mortar and pestle.

Chemicals. Dilute sulphuric acid, cupric oxide, litmus paper.

Chemical Reaction, $H_2SO_4 + CuO \longrightarrow CuSO_4\downarrow + H_2O$

Procedure. (*i*) Take 25 mL of dilute sulphuric acid in a 250 mL beaker. Add about 2 g of black cupric oxide powder. Heat gently and stirr with a glass rod. If all the oxide dissolve, add more. Start heating again. Continue to add until some oxide (total $\sim$5 g) is left in the liquid.

(*ii*) Filter the solution into an evaporating dish. Heat the solution gently on a sand bath and concentrate it to the saturation point (test the saturation point as described in Section 2.2).

(*iii*) Stop heating the solution and allow the solution to stand for crystallization.

(*iv*) After an interval of time, blue coloured crystals will appear. Decant off the mother liquor and wash the crystals with ice cold water to wash off the mother liquor adhering to the crystals. Dry the crystals by spreading them over a fold of filter papers (Fig. 2.6).

Results. Colour of the crystals = ...
Shape = ...
Yield = ...
Percentage yield = ...

Precautions. (*i*) The solution to be evaporated should be acid free. This is to be ascertained by a litmus paper. Undissolved cupric oxide also shows that no acid is left.

(*ii*) Do not concentrate the solution to dryness.

(*iii*) Gentle heating should be done to ensure uniform evaporation. Occasional stirring is advised.

(*iv*) Cool the hot saturated solution undisturbed.

(*v*) Do not concentrate the solution too much, as it will spit out of the dish as steam is formed beneath semi-solid parts of the mixture.

(*vi*) Do not boil the solution as spurting may occur.

(*vii*) To accelerate the process of crystallization and to get a large crystal a well shaped crystal should be added.

Note. One can purify the impure sample of copper sulphate by preparing a saturated solution of prepared impure sample of copper sulphate and then concentrating it to a saturation point as suggested in Section 2.2. The other details are given under Experiment 2.1.

Experiment 2.2. To prepare crystals of ferrous sulphate ($FeSO_4.7H_2O$) by reacting iron filings with dilute sulphuric acid.

Apparatus. Same as in Experiment 2.1.

Chemicals. Iron filings, dilute sulphuric acid, potassium thiocyanate solution, litmus paper.

Chemical Equation. $Fe + H_2SO_4 \longrightarrow FeSO_4 \downarrow + 2H$

Procedure. (*i*) Take 25 mL of dilute sulphuric acid in a 250 mL beaker. Add about 2 g of good quality iron filings (total iron filings 5 g). Heat gently so that the iron reacts with the acid and liberates hydrogen (nascent) gas which will reduce the ferric sulphate, if formed during the course of reaction, to ferrous sulphate. If all the iron filings dissolve, add more. Keep heating the contents. Continue to add until some iron filings are left in the solution.

(*ii*) When no more iron filings dissolve, filter the solution into an evaporating dish. Evaporate the filtrate on a sand both and concentrate it to the saturation point. Put drops of hot solution on a glass slide. If light green bits form, the saturation point has been reached.

(*iii*) Stop heating the solution. Leave it aside to form crystals. If necessary place it in an ice cold water bath for about half an hour.

(*iv*) After a short while, light green crystals will appear. Decant off the mother liquor. Wash the crystals to remove any mother liquor adhering to the crystals. Dry the crystals by spreading over a fold of filter papers.

Note. 1. The presence of ferric salts can be tested by treating a few drops of solution with potassium thiocyanate. The formation of red coloration shows the presence of ferric salt. Addition of iron filings to the stage when no more of them dissolves will ensure the absence of ferric salts.

2. Crystals of ferrous sulphate can also be obtained from Kipp's waste, a solution of mainly ferrous sulphate containing unreacted sulphuric acid. Excess of sulphuric acid is consumed by adding iron filings. The other details are as given above. On concentrating the solution to the point of crystallization and cooling, pale green crystals of the hepta-hydrate are deposited.

Result. Colour of the crystals =......
Shape =......
Yield =......
Percentage yield =......

Precautions. Same as in Experiment 2.1.

Experiment 2.3. To prepare crystals of ferrous ammonium sulphate or Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$.

Apparatus. Same as in Experiment 2.1.

Chemicals. Ferrous sulphate crystals, ammonium sulphate crystals, dilute sulphuric acid, distilled water.

General. When solutions of $FeSO_4.7H_2O$ and $(NH_4)_2SO_4$ are mixed in equimolecular proportions, crystals of double salt separate on concentrating and cooling the mixture. The crystals are characterized by their light green colour. They are transparent in nature. They are soluble in water. The aqueous solution is acidic in nature.

$$\underset{278}{FeSO_4.7H_2O} + \underset{132}{(NH_4)_2SO_4} \longrightarrow \text{Mohr's salt} + H_2O$$
$$\text{(Molecular masses)}$$

Procedure. (*i*) Dissolve the weighed $FeSO_4$ (10 g) and $(NH_4)_2SO_4$ (5 g) in about 10 mL distilled water contained in two separate beakers. Add 2-3 mL of dilute H_2SO_4 to prevent the hydrolysis of iron salt. Heat the solutions to boiling. Filter the solutions if there is any impurity.

(*ii*) Mix the two hot solutions. Pour the total solution into a china dish and concentrate the solution to a crystallization point.

(*iii*) Stop heating the solution. Leave in aside to form crystals. If necessary place it in an ice cold water bath for about half an hour.

(*iv*) After a short while, light green crystals will appear. Decant off the mother liquor. Wash the crystals with alcoholic water to remove any mothor liquor adhering to the crystals. Dry the crystals by spreading over a fold of filter papers.

Result. Colour of the crystals =.....
Shape =.....
Yield =.....
Percentage yield =.....

Precautions. (*i*) Dilute sulphuric acid should be added to a solution of ferrous sulphate to prevent its oxidation to ferric sulphate by atmospheric oxygen.

(*ii*) Don't heat the solution for long as it may oxidize ferrous ions to ferric ions.

(*iii*) If the solution turns yellow on concentration, discard the contents.

(*iv*) Other precautions are same as in Experiment 2.1.

Experiment 2.4. To prepare the crystals of potash alum (Fitkari), K_2SO_4, $Al_2(SO_4)_3.24H_2O$.

Apparatus. Same as in Experiment 2.3.

Chemicals. Potassium sulphate crystals, aluminium sulphate crystals, distilled water.

General. The crystals of potash alum are prepared by mixing the saturated solutions (containing equimolecular quantities) of potassium sulphate (K_2SO_4) and aluminium sulphate ($Al_2(SO_4)_3.18H_2O$). Transparent octahedral crystals of alum appear on cooling. It dissolves in water. Its aqueous solution is acidic in nature.

$$\underset{174}{K_2SO.} + \underset{666}{Al_2(SO_4)_3.18H_2O} + 6H_2O \longrightarrow \text{Potash alum}$$

(Molecular masses)

Procedure. (*i*) Dissolve the weighed potassium sulphate (2g) and aluminium sulphate (8 g) in about 20 mL distilled water contained in two separate 250 mL beakers. Stir well to dissolve the salts. Aluminium sulphate is not very soluble in cold water. Heat the contents to obtain a clear solution (if necessary add more water). A few drops of conc. H_2SO_4 is also added before heating the contents as it prevents the hydrolysis of $Al_2(SO_4)_3$.

(*ii*) Pour the two samples of solutions into a china dish. Heat the solution gently to crystallization point on a water bath (or sand bath).

(*iii*) Now stop heating the solution. Keep it aside to form crystals. If necessary place it on ice cold water bath for about half an hour.

(*iv*) On standing and cooling crystals will appear. Decant off the mother liquor. Dry the crystals by spreading over a fold of filter papers.

Result. Colour of the crystals =........
Shape ,, ,, ,, =........
Yield ,, ,, ,, =........
Percentage yield ,, =........

Precautions. (*i*) A few drops of conc. H_2SO_4 should be added while preparing a saturated solution of $Al_2(SO_4)_3$ to avoid hydrolysis. In the absence of acid, the solution becomes turbid.

(*ii*) Other precautions same as in Experiment 2.1.

ORAL QUESTIONS AND ANSWERS

Q. 2.1. What is the meaning of purity of a chemical substance ?

Ans. A pure substance is a single substance with definite melting point and other properties.

Q. 2.2. Explain the meaning of these words : solvent, solute, solution, soluble, saturated and crystals.

Ans. Solvent. It can keep the solute, *i.e.*, a soluble substance in solution. It is the major component of a solution.

Solute. A substance which disperses in the solvent. It is the minor component of a solution.

Solution. A homogeneous mixture of a solvent and solute.

Soluble. A substance is said to be soluble when it disperses into the solvent making a clear solution.

Saturated. A solution is said to be saturated which cannot dissolve the solute after a certain stage and at a given temperature. Here in the solution the dissolved solute is in equilibrium with the solid solute.

Crystals. Substances which have a regular arrangement of particles and thus a definite geometric shape.

Q. 2.3. What is the meant by crystallization ?

Ans. When a hot saturated solution of a salt is allowed to cool slowly, the salt starts separating out in the form of crystals. This process is known as crystallization.

Q. 2.4. Why do crystals form when hot solution is cooled ?

Ans. From hot solution, on cooling, initially some bits of salt come out. Around these bits, more of bits start depositing forming crystals.

Q. 2.5. Does hot water as compared to cold water dissolve more solute or less ?

Ans. Hot water dissolves more solute, because its tendency toward randomness increases because of the increased energy on heating.

Q. 2.6. Why is the solution not concentrated too much or evaporated to dryness in the preparation of crystals ?

Ans. When the solution becomes very concentrated, it will spit out of the dish as steam is formed beneath semi-solid parts of the mixture. Also we get poor quality crystals.

Q. 2.7. What is seeding ?

Ans. Sometimes the process of crystallization becomes very slow. In such cases, a well shaped crystal of the salt is suspended in the concentrated solution. Around this crystal, more bits of salt deposit. This is known as seeding.

Q. 2.8. Which of the two techniques is more efficient : decantation or filtration ?

Ans. Filtration is more efficient because it removes even the fine particles suspended in a liquid medium.

Q. 2.9. What is an unsaturated solution ?

Ans. An unsaturated solution is one which can take more of the solute at that temperature.

Q. 2.10. What is a crystal ?

Ans. The solid form of a particle having regular geometrical shape is named as crystal.

Q. 2.11. What is decantation ?

Ans. The process of separating insoluble substances from a liquid by simply allowing it to stand for some time and then pouring off the mother liquor.

Q. 2.12. What is distillation ?

Ans. The combined process of evaporation and condensation is termed as distillation.

Q. 2.13. What is evaporation ?

Ans. Evaporation is a process in which a liquid is converted into its vapour either by exposure to air at ordinary temperature or by the application of heat.

Q. 2.14. List the factors that influence solubility.

Ans. (*i*) Nature of the solute and solvent,
(*ii*) Temperature, and
(*iii*) Pressure.

Q. 2.15. What is mother liquor ?

Ans. The liquid which is left after crystals are separated from the saturated solution is called the mother liquor.

Q. 2.16. What is blue vitriol ?

Ans. Hydrated copper sulphate ($CuSO_4.5H_2O$) is known as blue vitriol.

Q. 2.17. Will the aqueous solution of copper sulphate be acidic, basic or neutral ?

Ans. It will be acidic.

Q. 2.18. What is green vitriol ?

Ans. Hydrated iron (II) sulphate, $FeSO_4.7H_2O$ is called green vitriol.

Q. 2.19. What is Kipp's waste ?

Ans. It is a solution of mainly ferrous sulphate with unreacted sulphuric acid in Kipp's apparatus in which H_2S is produced by the reaction of iron (II) sulphide with dilute sulphuric acid.

Q. 2.20. Why do the green crystals of ferrous sulphate turn brown on exposure to air ?

Ans. Due to its oxidation to basic ferric sulphate.

$$\underset{\text{(Green)}}{4FeSO_4} + 2H_2O + O_2 \longrightarrow \underset{\text{(Brown)}}{4Fe(OH)\,SO_4}$$

Q. 2.21. What is efflorescene ?

Ans. Certain substances on exposure to air lose their water of crystallization. This property of the substance is known efflorescence.

Q. 2.22. How will you calculate the % purity of substance (or percentage of each substance) in the mixture ?

Ans. By using the formula given below :

$$\%\text{ component} = \frac{\text{Grams of component} \times 100}{\text{Grams of sample}}$$

Q. 2.23. Calculate the theoretical mass of copper sulphate obtainable from a given amount of cupric oxide.

Ans. Theoretical mass of copper sulphate

$$= \text{Wt. of CuO} \times \frac{\text{Gram formula mass of } CuSO_4.5H_2O}{\text{Gram formula mass of CuO}}$$

$$\%\text{ yield} = \frac{\text{Mass of } CuSO_4.5H_2O \text{ obtained}}{\text{Theoretical mass of } CuSO_4.5H_2O \text{ from the given amount of CuO}} \times 100$$

Q. 2.24. What is potash alum ? Is it a double salt or complex compound ?

Ans. The chemical formula for potash alum is $K_2SO_4.Al_2(SO_4)_3.24H_2O$.

Potash alum, and other alums, are double salts. Potash alum on dissolving into water furnishes K^+, Al^{3+} and SO_4^{2-} ions which can be tested by their usual tests.

Q. 2.25. What is the nature of aqueous solutions of potash alum and Mohr's salt ?

Ans. Acidic.

Q. 2.26. 'The crystals of alums grow easily'. Comment on the statement.

Ans. Alums are sparingly soluble in cold water. Because of this property, their crystals grow easily.

Q. 2.27. How does potash alum help in the purification of water ?

Ans. Dust particles being negatively charged are coagulated by Al^{3+} ions. As a result, the dust particles settle down making water clear.

Q. 2.28. Why is the concentration of solution not done for long in the preparation of crystal ?

Ans. Long heating give poor quality crystals.

Q. 2.29. What is Mohr's salt ?

Ans. $FeSO_4.(NH_4)_2SO_4.6H_2O$.

Q. 2.30. Name the ions present in a solution of Mohr's salt.

Ans. Mohr's salt when dissolved in water forms a clear solution which contains Fe^{2+}, NH_4^+ and SO_4^{2-} ions. These ions can be tested by their usual tests.

Q. 2.31. In the preparation of ferrous sulphate solution for the preparation of Mohr's salt, a few drops of sulphuric acid are added. Comment

Ans. To prevent the hydrolysis and oxidation of ferrous sulphate.

Q. 2.32. What is meant by equimolecular proportion ?

Ans. When two substances are mixed in the ratio of their molecular masses, they are said to be present in equimolecular proportion.

Q. 2.33. At times Mohr's salt crystals are washed with alcohol. Comment.

Ans. To remove sulphuric acid from Mohr's salt crystals.

Q. 2.34. Why is Mohr's salt used in place of ferrous sulphate in the titrimetric analysis ?

Ans. Mohr's salt is a primary standard. Fe^{2+} ions do not get oxidized by atmospheric oxygen.

Q. 2.35. How does an aqueous solution of ferric alum or $FeCl_3$ stop blood coming out from a cut ?

Ans. Blood contains certain negatively charged particles. Fe^{3+} ions neutralize these particles and thus help in coagulation of blood. Finally the blood clots.

Q. 2.36. Aluminium hydroxide is insoluble in water but is soluble in excess of alkali. Comment.

Ans. Due to the formation of meta-aluminate.

$$\underset{\textbf{(Insoluble)}}{Al(OH)_3} + NaOH \longrightarrow \underset{\textbf{(Soluble)}}{NaAlO_2} + 2H_2O$$

Q. 2.37. How does a double salt differ from a complex salt ?

Ans. A complex salt does not furnish the ions of its constituents when contained in solution whereas a double salt does. For example, $K_4[Fe(CN)_6]$ does not give tests for Fe^{2+} ions but Mohr's salt solution gives the test for Fe^{2+} ions.

□ □

UNIT 3

Sols : Preparation, Purification and Coagulation

3.1. INTRODUCTION

A colloidal system is always heterogeneous and consists of at least two phases : the **dispersed phase** (the phase constituting the colloidal particles) and the **dipersion medium** (the medium in which these colloidal particles are dispersed).

To name any system as colloidal, size of the dispersed particles is the primary criterion. The various colloidal solutions (systems) are compared with true solutions on one hand and those of suspensions on the other.

A **true solution** is a homogeneous mixture of dispersed phase and dispersion medium, *e.g.*, sugar, table salt, *etc.*, dissolve in water and constitute (one phase) true solution. Solute and the solvent cannot be separated into their original forms. Naphthalene in benzene, soap in alcohol, *etc.*, also constitute true solutions.

A **suspension** is a heterogeneous mixture of a dispersed phase and dispersion medium, *e.g.*, sand, powdered glass, *etc.*, in water behave as suspensions. Solute particles settle at the bottom due to their large size. Solute and solvent can be separated easily by some physical means. Clay in water, $PbSO_4$ in water, *etc.* also represent suspensions.

The size of the particles which form true solutions is less than 10^{-7} cm while the size of the particles which form suspensions is greater than 10^{-4} cm. The intermediate state between these two is known as the **colloidal state.**

Both the dispersed and the dispersion medium can be solid, liquid or gas, although the most commonly occurring dispersions are those of solids in liquids (sols) and liquids in liquids (emulsions). Colloidal dispersions are thermodynamically unstable and cannot be readily reconstituted after the two phases have been separated.

3.2. LYOPHILIC AND LYOPHOBIC SOLS

Colloidal dispersions of solids in liquids, *i.e.*, sols are of two different kinds. In one case the solid has an attraction for the liquid and disperses spontaneously in it. In the other case, the solid and liquid are not attracted to each other and the resultant sol resembles the pure liquid in many of its properties, *e.g.*, viscosity and surface tension. The former are called **lyophilic (solvent loving) sols** and the latter **lyophobic (solvent-hating) sols**. If water is the dispersion medium, they are termed **hydrophilic** and **hydrophobic sols** respectively.

Sols of metals (*e.g.*, gold and silver sols), metehydroxides, oxides and sulphides (*e.g.*, arsenic sulphide sol), oils, fats *etc* , in water are examples of lyophobic sols. These sols are easily precipitated on the addition of small amount of electrolytes, by heating or agitation. They are preserved by adding stabilizing agents. They are irreversible sols.

Sols of starch, gum, albumin, gelatin, *etc.* in water are examples of lyophilic sols. There sols are quite stable, *i.e.*, require no stabilizer. In these sols, the dispersed phase is not easily precipitated because of strong attractive forces operating between the suspended particles and the dispersion medium. After precipitation, they can be easily reverted to the colloidal state on shaking with the dispersion medium. They are reversible in nature.

3.3. PREPARATION OF SOLS

Colloids can be prepared by one of two general methods.

(I) Dispersion methods

In these methods large particles are broken down to a colloidal size in the dispersing phase by some appropriate mechanical means, *e.g.*, in a colloid mill or subjected to ultrasonic dispersion. These unstable solutions are stabilized with a stabilizer.

There methods lead to aggergation as well as dispersion. Aggergation is effected by the mechanical forces used in the grinding process, and partly by the forces of attraction between the particles. The aggregation process can be reduced by addidg a solid, inert diluent, such as glucose. This can later be removed by **dialysis**.

Sometimes the aggregates are dispersed to the colloidal state when shaken with water containing a very small amount of an electrolyte (called peptizing agent). This process is termed **peptization**. For example, the sol of AgCl can be prepared by peptizing it with either an aqueous solution of $AgNO_3$ or KCl.

Sols of starch, gum or egg albumin can also be obtained by dispersion method. At times heating is also helpful in accelerating the dispersion, *e.g.*, in the preparation of starch sol.

(II) Condensation methods

Through these methods, molecules or ions join together to give insoluble particles of colloidal size. Condensation can occur by physical or chemical means

Chemical methods

In chemical methods some chemical reactions are involved; one of the products formed in reaction is normally insoluble in the dispersing medium. Insoluble product does not coagulate but remains dispersed as colloid. Some of the reactions generally involved are oxidation, reduction, hydrolysis and double decomposition. Sulphur sol is prepared by the oxidation of H_2S water using SO_2.

$$\underset{}{H_2S(aq)+SO_2(g) \rightarrow 2H_2O+\underset{\text{(Sol)}}{3S}}$$

Physical methods

(*i*) **By exchange of solvent :** Phosphorus and sulphur are highly soluble in alcohol but insoluble in water. Their colloidal sols can be prepared by pouring their alcoholic solutions drop by drop into water. Alcohol is removed by dialysis. A milky colloidal solution of phenolphthalein indicator results when its alcoholic solution is poured into water. Such solutions are unstable.

(*ii*) **By change in physical state :** Sols of mercury and sulphur are produced by passing their vapours through cold water. Ammonium citrate is mixed to stabilize the solution.

(*iii*) **By controlled condensation :** Certain insoluble substances give colloidal solutions by their precipitation in the presence of some protective colloidal systems (*e.g.*, starch, gelatin, glycerol, glucose, *etc*). Prussian blue sol is produced by precipitating it in the presence of starch.

3.4. PURIFICATION OF SOLS

Impurities present in sol make the sol unstable. It is necessary to reduce their concentrations in a judicious way. The purification of sol may be effected by (*i*) dialysis or (*ii*) ultrafiltration. **Dialysis** is the process of dissolved particles of substances from a sol by means of diffusion through membranes made of parchment paper, cellulose nitrate, cellophane, *etc*. The membrane is termed semipermeable as it permits the passage of one type of particles. The sol is filled in the membrane bag suspended in pure water (Fig. 3.1). It allows the small ions of dissolved electrolytes (or substances) to pass through but retains the colloidal particles. It is a slow process which can be speeded up by using warm water. The dialysis can be further accelerated by applying a potential difference across the membrane. Under the influence of electric field, ions migrate at a much faster rate than in a simple dialysis. At times, the container is divided into three compartments. The middie compartment (made of semipermeable membrane) is filled with sol and the other two are filled with pure water.

Ultrafiltration is a filtration process where an ultrafilter—a filter device with reduced pore size is used. This allows the passage of dissolved electrolytes (or substances) and the dispersion medium

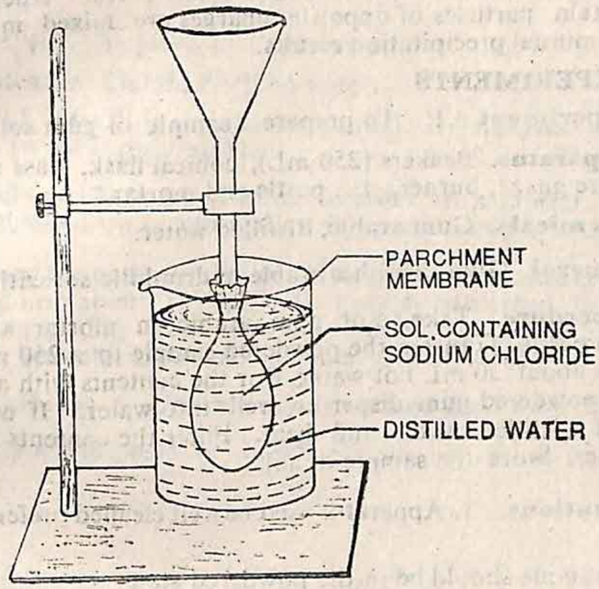


Fig. 3.1. Purification of sol by dialysis.

but not the colloidal particles. An ordinary filter paper impregnated with colloidion or gelatin solution serves the purpose. Sintered glass, unglazed gorcelain, *etc*., can also be used as ultrafilters. Ultrafilters of different pore sizes help in separating fractions containing particles of different sizes. Slime on treating with water disperses spontaneously to give a sol.

3.5. COAGULATION OF SOLS

Neutralization of the charges on the colloidal particles of a lyophobic sol results in the aggregation or coalescing of the particles to form a visible precipitate, the phenomenon being known as coagulation. High concentration of electrolytes is effective in neutralizing the charge on the colloidal particles, *i.e*., in aggregating the particles and hence in coagulation. The principles governing the coagulation of sols by electrolytes are contained in the Hardy-Schulze law which states that :

(*i*) the coagulation of colloidal particles is brought about effectively by the ions carrying opposite charge to that of colloidal particles.

(*ii*) the coagulating power of an ion increases appreciably with increase in charge on ions causing coagulation.

Thus a positive sol like ferric hydroxide sol is coagulated by anions like NO_3^-, SO_4^{2-}, *etc.* and a negative sol like As_2S_3 sol is coagulated by cations like K^+, Ba^{2+}, Al^{3+}, *etc*. When two sols which cotain particles of opposite charges are mixed in equivalent amounts mutual precipitation results.

3.6. EXPERIMENTS

Experiment 3.1. To prepare a sample of gum sol.

Apparatus. Beakers (250 mL), conical flask, glass rod, tripod stard, wire guaze, burner, *etc* , pestle and mortar.

Chemicals. Gum arabic, distilled water.

General. Gum furnishes stable hydrophilic sol with water.

Procedure. Take 5g of gum arabic in mortar and grind it well with pestle. Transfer the powdered sample to a 250 mL beaker. Now add about 50 mL hot water. Stir the contents with a glass rod, until the powdered gum disperses well into water. If needed add more of distilled water and heat. Filter the contents through a filter paper. Store the sample of sol.

Precautions. 1. Apparatus used be well cleaned preferably steam cleaned.

2. Sample should be in the powdered state.

Experiment 3.2. To prepare a sample of egg albumin sol.

Apparatus. Same as in Experiment 3.1.

Chemicals (or materials). 2 eggs, distilled water.

General. Egg albumin disperses well into water and forms hydrophilic sol. It is quite stable and is not affected by electrolytic impurity.

Procedure. Take the eggs and break their shells by striking gently against the hard surface or with the end of a spatula or spoon. Pour the colourless liquid along with yellow yolk into a beaker. Decant off the colourless liquid known as egg albumin carefully into another well cleaned beaker.

Now start adding the clear liquid of egg albumin in small instalments to distilled water (~ 50 mL) contained in a beaker with constant stirring. Filter the sol through a filter paper and store it well.

Precautions. 1. The operation of adding egg albumin to water should take at least 30 min.

2. Only cold distilled water should be used. In hot water coagulation of egg albumin takes place.

Experiment 3.3. To prepare the sample of starch sol.

Apparatus. As given in Experiment 3·1.

Chemicals. Starch, distilled water.

General. Starch is an intrinsic colloid. It disperses well into hot water. Its sol is quite stable.

Procedure. Take 1 g of starch powder in a mortar. Add a few mL of distilled water and make a fine paste using pestle.

Now pour the paste (preferably after taking into a beaker) along the glass rod into about 100 mL boiling water contained in a 250 mL conical flask (Fig. 3.2). Boil the contents for about 2—3 min and allow to get cold. Label the contents at 'starch sol.'

Precautions. 1. Use thoroughly cleaned glass ware (Fig. 3.3).

2. Only a fine paste of starch should be added to boiling water.

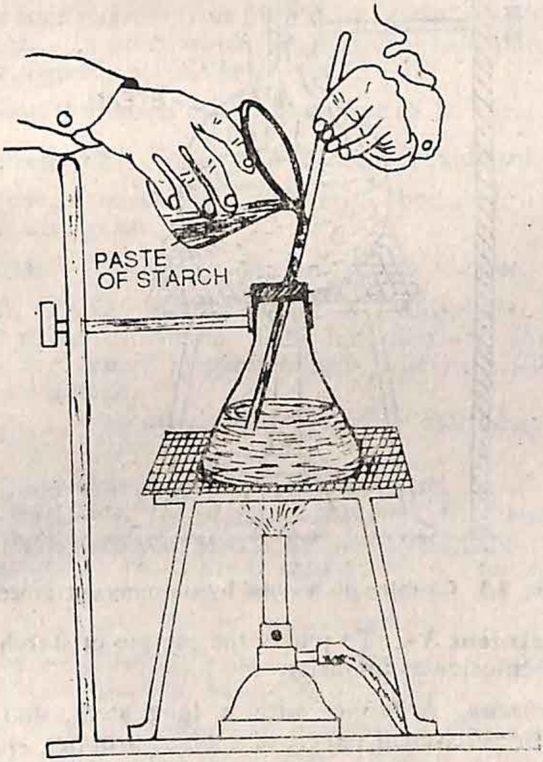


Fig. 3.2. Preparation of starch sol.

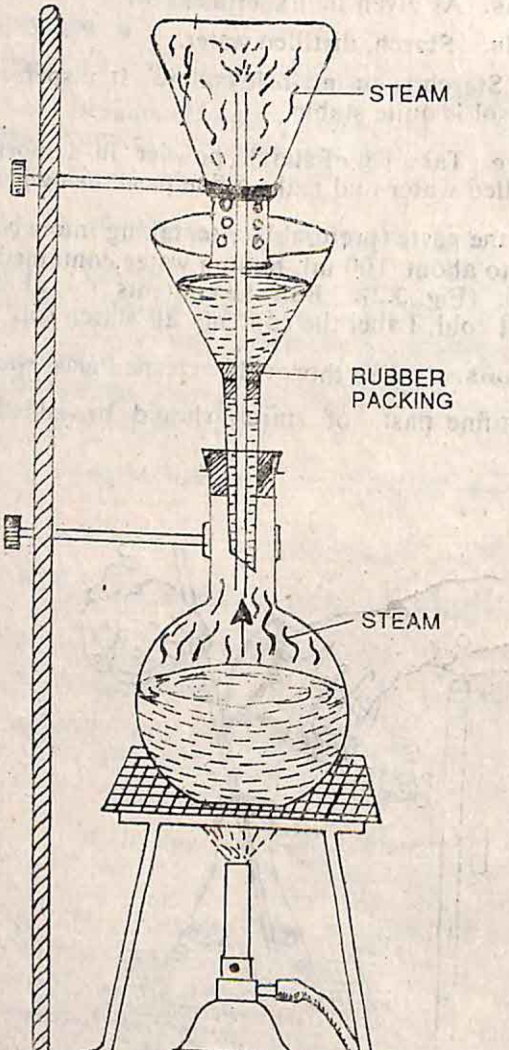


Fig. 3.3. Cleaning of a vessel by steaming out process.

Experiment 3·4. To purify the sample of starch sol containing sodium chloride as impurity.

Apparatus. A funnel with a long stem, 400 mL beaker, cellophane or parchment paper, test tubes, dropper, *etc.*

Chemicals. Starch sol containing sodium chloride, silver nitrate solution and iodine solution.

General. The basic principle of the purification of sols by dialysis is that the colloidal particles do not pass through the cellophane or the parchment paper as they are bigger in size whereas the molecules or ions of the electrolyte (NaCl) being small in size pass through.

Procedure. Fold the parchment paper in such a way as it assumes the shape of bag and fix it on to the stem of a funnel with the help of thread. Now fill the parchment bag with impure starch sol to it 2/3 capacity. Immense the bag into distilled water contained in a beaker (Fig. 3·1). Change the water at regular intervals.

Take out a few drops of water with a dropper in a test tube. Add a few drops of iodine solution. In case, blue colour does not appear, the water is starch free.

Again take out a few drops of water from the beaker with a dropper in a test tube. To it add $AgNO_3$ solution. A white turbid solution due to AgCl ensures the presence of Cl^- ions.

Chloride ions migrate from starch sol by diffusion through the parchment paper. In other words, we may conclude that $Na+$ and Cl^- diffuse through the parchment paper.

As a result, the starch sol becomes free of Na^+ and Cl^- ions.

Experiment 3.5. To prepare ferric hydroxide sol.

Apparatus. Conical flasks (250 mL), boiling test tube, dropper, glass rod, wire guaze, *etc*.

Chemicals. Ferric chloride solid, distilled water.

General. Ferric hydroxide sol is hydrophobic in nature. We know that ferric hydroxide does not disperse in the water thoroughly. It is prepared by condensation method. Condensation is effected by hydrolysis.

$$FeCl_3\,(aq) \rightarrow 3H_2O(l) \rightarrow Fe\,\underset{(Sol)}{(OH)_3}\,(s) + 3HCl\,(aq)$$

$Fe(OH)_3$ molecules undergo agglomeration to give particles of colloidal dimensions. These particles adsorb Fe^{3+} ions from the solution and thus, acquire positive charge. Due to the presence of these positive charges, particles are repelled from one another and thus they never approach close enough so as to coalesce and get precipitated. As a result, the sol. becomes stable.

Procedure. Clean the glass apparatus, *viz*., conical flask, test tube, *etc*. with the steam jet as suggested in Fig. 3.3.

Prepare ~10 mL saturated solution of ferric chloride in distilled water. Now start adding ferric chloride solution drop by drop with the help of a dropper to the boiling water (~100 mL) contained in a conical flask until a deep wine red sol of ferric chloride is obtained. Heat the contents for sometime to ensure the complete hydrolysis.

The rod sol of ferric hydroxide contains hydrochloric acid as an impurity. It can be removed by dialysis process using a parchment or cellophane bag as discussed in Section 3.4.

Precautions. (*i*) Ensure about the cleanliness to apparatus to prevent the coagulation of sol Ionic impurities help the process of coagulation.

(*ii*) Ensure the removal of HCl, otherwise it may restabilize the sol.

Experiment 3.6. To prepare aluminium hydroxide sol.

Hint. Aluminium hyroxide sol is also hydrophobic in nature. It is obtained by adding a saturated solution of aluminium cholo-ride to boiling water.

$$AlCl_3 + 3H_2O \rightarrow \underset{\text{(Sol)}}{Al(OH)_3} + 3HCl$$

The other details are as given in Experiment 3.5.

Experiment 3.7. To prepare a sample of arsenic sulphide sol.

Apparatus. Two 400 mL beakers' 400 mL conical flasks, Kipp's, apparatus, burner, etc.

Chemicals. Arsenious oxide (As_2O_3), distilled water, iron pyrites, dil H_2SO_4.

General. $As_2O_3\,(aq) + H_2S(g) \rightarrow \underset{\text{(sol)}}{As_2S_3}\,(aq) + 3H_2O\,(l)$

Procedure. Clean the glass apparatus by a steam jet. Now put 1.0–1.5 g to As_2O_3 in ~ 250 mL distilled contained in a 400 mL beaker. Heat the contents with constant stirring until the entire amount of arsenious oxide dissolves. Stop heating and cool the solution. If the solution is not clear, filter and pass H_2S gas through the solution. Pass H_2S gas until the opalescent solution assumes yellow colour. (Fig. 3.4). Continue to pass H_2S gas until the solution assumes permanent yellow colour and the intensity does not change.

Now pass CO_2 or H_2 gas through the turbid yellow liquid to remove excess of H_2S. The gas is passed for such a time until the escaping gas does not turn lead acetate paper black. If H_2S gas is not removed, a partial precipitation of the sol may occur.

Filter the sol through a fluted paper and collect the sol in another beaker.

Dialyse the sol by using a parchment paper as described in Section 3.4 and Experiment 3.4.

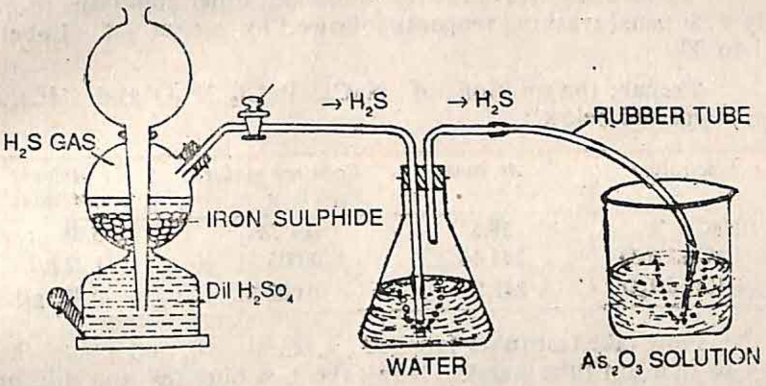


Fig. 3.4. [Preparation of AS_2S_3 sol by passing H_2S gas through AS_2O_3 solution.

Precautions. (*i*) Glass apparatus should be washed thoroughly with steam jet.

(*ii*) H_2S gas should be passed after passing through water trap to free it from the impurities from Kipp's apparatus.

Experiment 3.8. To compare the precipitating powers of sodium chloride (NaCl), barium chloride ($BaCl_2$) and aluminium chloride ($AlCl_3$) for precipitating negative arsenious sulphide (As_2S_3) sol.

Apparatus. Test tubes with stoppers, burettes, test tube stand.

Chemicals. As_2S_3 sol sodium chloride, barium chloride aluminium chloride, distilled water, *etc*.

General. The precipitating power of an electrolyte is the minimum number of milimoles of it present in one litre of the sol and just sufficient to cause coagulation of a sol. This amount of electrolyte is called its coagulation value. The amount of an electrolyte required to coagulate a fixed amount of sol depends upon the charge on the ion responsible for coagulation.

As arsenious sulphide sol is negatively charged, it can be precipitated by positively charged ions, *i.e.*, cations (*e.g.* Na^+ in NaCl, Ba^{2+}in $BaCl_2$ and Al^{3+} in $AlCl_3$). According to the Hardy-Schulze law, the higher the charge on the ion, the higher is its precipitation value. Thus, the precipitation values of these ions for arsenious sulphide sol are in the order of $Al^{3+} > Ba^{2+} > Na^+$.

In view of the Hardy-Schulze law the solution of Al^{3+} should be of low concentration as compared to Ba^{2+} and Na^+ and that of Ba^{2+} should be of low concentration as compared to Na^+.

Procedure. Wash the test tubes and other apparatus thoroughly with usual washing reagents followed by steam jet. Label them 1 to 30.

Prepare the solutions of NaCl, $BaCl_2.2H_2O$ and $AlCl_3.6H_2O$ as suggested below :

Electrolyte	*At. mass*	*Required molarity*	*Amount required*
NaCl	58.5	0.1 M	5.85 g/L
$BaCl_2.2H_2O$	244.44	0.005 M	1.22 g/L
$AlCl_3.6H_2O$	241.5	0.002 M	0.483 g/L

Now take test tubes labelled 1, 2, 3......10, and place them in a row in a test tube stand. Now take two burettes and fill one of them with distilled water and the other with 0.1 M NaCl solution.

Measure out different volumes say 1, 2, 3,......10 mL of 0.1M NaCl solution in test tubes labelled 1, 2, ...10 respectively. Make up the total volume 10 mL in each of them by adding distilled water.

Now add 5 mL of freshly prepared pure sample of As_2S_3 sol Experiment 3.7) in each of the test tubes with the help of a burette. Stopper them and mix the contents in them by just inverting them (Fig. 3·5). Allow them to stand for about 30 min or more.

Now examine each test tube against a dark background and mark the test tubes in which turbidity appears. Record the observations as suggested in Table 3.1.

Table 3.1

Test tube	*Volume of 0.1 M NaCl* (mL)	*Volume of distilled water* (mL)	*Volume of As_2S_3 sol* (mL)	*Observations*
1	1.0	9.0	5.0	↑
2	2.0	8.0	5.0	
3	3.0	7.0	5.0	Appearance of turbidity is to noted.
4	4.0	6.0	5.0	
5	5.0	5.0	5.0	
6	6.0	4.0	5.0	
7	7.0	3.0	5.0	
8	8.0	2.0	5.0	
9	9.0	1.0	5.0	
10	10.0	—	5.0	↓

Repeat the experiment in a similar manner by taking $BaCl_2.2H_2O$ and $AlCl_3.6H_2O$ solutions in test tubes marked as 11, 12,...20 and 21, 22,......30 respectively.

At times it is difficult to judge whether the precipitation or coagulation has started or not. This can be determined by comparing the test tube containing the electrolyte and the sol with the one which only contains the sol.

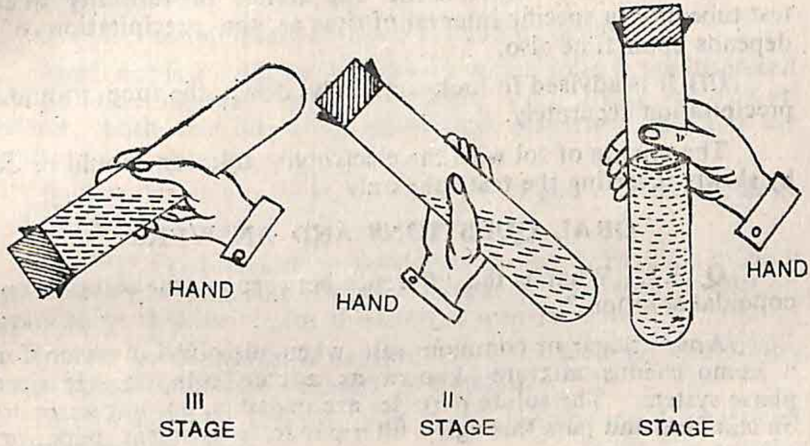


Fig. 3.5. Inverting the sol to which electrolyte has been added.

Calculation. Let the volume of 0·1 M NaCl for precipitating the sol is $=v\text{mL}^2$

$$\therefore \text{ Number of moles of NaCl present per mL} = \frac{0.1}{1000}$$

$$\text{or Number of milimoles of NaCl present per mL} = \frac{0.1}{1000} \times 1000 = 0\cdot1$$

Number of milimoles of NaCl present in v mL of NaCl solution $=0.1 \times v$

$$\text{Precipitation value} = \frac{0.1 \times v \times 1000}{10 \text{ (volume of mixture)}}$$

Note. The experiment can also be performed by taking 5 mL of arsenious sulphide sol in a conical flask and adding dropwise NaCl or $BaCl_2$ or $AlCl_3$ solution from the burette. Initially the solution will be clear, then it starts becoming turbid and finally becomes opaque with the setting of the As_2S_3 precipitate. The minimum volume of the electrolyte required to precipitate As_2S_3 sol is noted and the precipitation value is calculated.

Similarly, the precipitation values can be determined and compared with other electrolytes.

Result. On comparing the precipitation power or value of NaCl, $BaCl_2.2H_2O$ and $AlCl_3.6H_2O$, the trend is found to be

$$AlCl_3 > BaCl_2 > NaCl.$$

Precautions. (*i*) Note the appearance of turbidity in each test tube after a specific interval of time as the precipitation of sol depends upon time also.

(*ii*) It is advised to look vertically down the tube to find the precipitation accurately.

The mixing of sol with the electrolyte solution should be done by slowly inverting the test tube only.

ORAL QUESTIONS AND ANSWERS

Q. 3.1. What is the difference between a true solution and a colloidal solution ?

Ans. Sugar or common salt when dissolved in water forms a homogeneous mixture known as a true solution. It is a one phase system. The solute particles are invisible, do not settle down on standing and pass through a filter paper, parchment paper or an animal membrane.

In a colloidal solution, the colloidal particles are found dispersed in a dispersing phase. It is always a two-phase heterogeneous system. The solute particles can only be seen through microscope. They diffuse through a parchment membrane.

Q. 3.2. Define lyophilic and lyophobic sols.

Ans. Collodial particles having strong affinity for the dispersion medium constitute lyophilic sols, *e.g.*, starch gelatin, ghee, proteins, *etc.* and colloidal particles with apparent affinity for the dispersion medium constitute lyophobic sols *e.g.*, sols of metals, metal hydroxides and metal sulphides.

(For details refer to Pathways of Chemistry, Vol. 2 by Dr. D.P. Goel p. 749 and 750).

Q. 3.3. What is the size of particles in true solution, colloidal solution and suspension ?

Ans.		
	True solution	1.0 nm
	Colloidal solution	range from 1.0—100 nm
	Suspension	range from 100—500 nm

Q. 3.4. Classify the following into lyophilic and lyophobic sols.

(*i*) Gum sol, (*ii*) Fe $(OH)_3$ sol, (*iii*) Starch sol, (*iv*) As_2S_3 sol. and (*v*) $Al(OH)_3$ sol.

Ans.

Lyophilic	**Lyophobic**
gum sol	$Fe(OH)_3$ sol, As_2S_3 sol
starch sol	$Al(OH)_3$ sol

Q. 3.5. What is the charge on $Fe(OH)_3$ sol ?

Ans. Positive.

Q. 3.6. Differentiate between sol and emulsion.

Ans. Sol is a colloidal solution in which solid is the dispersed phase and liquid is the dispersion medium, *e.g.*, As_2S_3 sol. In an emulsion, both the dispersed phase and dispersion medium are liquids.

Q. 3.7. State a few reasons for the origin of electric charge on colloidal particles.

Ans. (*i*) Frictional electrification is caused by mutual rubbing of particles with molecules of dispersing phase. This sort of friction appears to be responsible for the charges over particles.

(*ii*) At times particles capture electrons from air and during electrodispersion method (Bredigs' Are method).

(*iii*) Preferential adsorption of ions common to the particles from the solution phase.

(*iv*) Dissociation of surface molecules.

(*v*) Dissociation of molecular electrolytes adsorbed on the surface of particles.

Q. 3.8. Why do adsorbed charges on colloidal particles act to prevent coagulation and precipitation of colloidal particles ?

Ans. All the particles in a particular colloidal dispersion carry the same charge, so the particles repel one another and do not coalesce into particles large enough to precipitate from the suspension.

Q. 3.9. Frequently a preparation of a colloid, such as a protein can be made more stable if the protein is dialyzed. Why is this so ?

Ans. This is because dialysis helps in removing undesirable ions from a colloidal preparation in order to stabilize the colloid.

Q. 3.10. Give examples of positively and negatively charged sols.

Ans. Positively charged sols

$Fe(OH)_3$, $Al(OH)_3$, TiO_2, proteins in acidic solution.

Negatively charged sols

Metallic sols of Au, Ag, *etc.*

Sulphur, As_2S_3, Gum egg albumin and starch sols.

Q. **3.11**. What will happen if an electrolyte is added to $Fe(OH)_3$ sol ?

Ans. The sol will be precipitated, because it is hydrophobic.

Q. **3.12**. Do colloidal particles separate from a sol on filtering, centrifuging or standing ?

Ans. No.

Q. **3.13**. What is the order for precipitating action of cations *e.g.*, Na^+, Ba^{2+}, Al^{3+} on negatively charged As_2S_3 sol.

Ans. It is in order of $Al^{3+} > Ba^{2+} > Na^+$.

Q. **3.14**. Name the methods employed in preparting the sols.

Ans. Condensation and dispersion methods.

Q. **3.15**. What is peptization ?

Ans. Peptization is the process by which certain substances (formed as a result of accumulation of colloidal size particles) are dispersed to the colloidal state when shaken with water containing very small amount of an electrolyte which acts as the peptizing agent.

Q. **3.16**. How does a colloidal solution acquire stability ?

Ans. It is because of setting up of a electrical double layer between the colloidal particles and the solution.

Q. **3.17**. Name the process generally used for the purification of sols ?

Ans. Dialysis.

Q. **3.18**. What is meant by 'dialysis' ? Is dialysis a slow process ?

Ans. The phenomenon of purification of sols by passing through a semi-permeable membrane is known as dialysis.

Yes, it is a slow process.

Q. **3.19**. What is the special characteristic of paper used in dialysis ? Name two such papers.

Ans. It permits only the electrolyte to pass through it and does not allow the passage of colloidal particles. Parchment and cellophane paper.

Q **3.20**. Does dialysis carry any significance in daily life ?

Ans. Kidney in our body functions on the principle of dialysis. Sewage disposal also works on this principle.

Q **3.21**. Comment on the diffusion of colloidal particles through parchment bag.

Ans. Colloidal particles, being larger in size than the pore's size of parchment paper, do not diffuse through parchment bag.

Q. 3.22. Comment on the colloidal particles always being found dispersed in colloidal solutions.

Ans. In lyophilic colloids the strong interaction between the dispersed phase and dispersion medium makes them stable. The lyophobic colloids, generally carry charge. It is the repulsion between the charged particles that make them stable.

Q. 3.23. Which of the two sols : lyophilic or lyophobic is more stable ?

Ans. Lyophilic.

Q. 3.24. What is coagulation ?

Ans. It is a process of changing the colloidal state into a large sized particles which finally settle down as a precipitate.

Q. 3.25. Why do colloidal particals remain suspended in colloidal solutions ?

Ans. The colloidal particles remain suspended in colloidal solution because of the following properties of colloidal particles.

(*i*) They are electrically charged.

(*ii*) They have a small size.

Q. 3.26. How are colloidal solutions coagulated ?

Ans. When colloidal particles come closer due to some reason, there occurs the coagulation of colloidal solutions.

Coagulation can be caused by heating and shaking the sols vigorously. Addition of an electrolyte also helps in the process of coagulation as it neutralizes the charge on the colloidal particles. Generally ions with opposite charge to that of colloidal particles are used. Ions with higher charges are more effective.

Q. 3.27. Do colloidal particles carry any charge ?

Ans. Yes, colloidal particles carry either +ve or —ve charge, but colloidal solutions are neutral.

Q. 3.28. How is the nature of a charge of a sol determined ?

Ans. By electrophoresis technique.

Q. 3.29. Why does a sol get coagulated, when brought into contact with an electrolyte ?

Ans. When an electrolyte is added to a colloidal system, ti neutralizes the charge on the colloidal particles and causes them to aggregate and grow in size to form a precipitate, thus coagulating the sol.

Q. 3.30. What do you understand by the precipitation value of an electrolyte ?

Ans. The precipitation value of an electrolyte for a specific sol is the minimum number of millimoles of the electrolyte present per litre of the total solution of the 'sol' and the electrolyte, which is just enough to initiate the process of coagulation.

Q. 3.31. While determining the precipitation value of different electrolytes, vigorous shaking is not advised. Comment.

Ans. Vigorous shaking causes the precipitation of the dispersed particles much faster.

Q. 3.32. What is Hardy-Schulze rule ?

Ans. The rule states that the precipitation power of an electrolyte depends upon the magnitudes of charge on a ion carrying an opposite charge to that of the dispersed phase.

Q. 3.33. If colloidal particles carry a positive charge, what will be charge on the particles of the dispersion medium ?

Ans. The dispersion medium has an equal and opposite charge to that of colloidal particles and thus makes the system neutral as a whole. For example, if colloidal particles have +ve charge, the particles of the dispersion medium will have the −ve charge each.

Q. 3.34. In which order does the precipitating action of ions : Cl^-, SO_4^{2-} and PO_4^{3-} on positively charged $Fe(OH)_3$ sol occur ?

Ans. In the order of $PO_4^{3-} > SO_4^{2-} > Cl^-$.

Q. 3.35. Colloidal solutions are always neutral. Comment.

Ans. Colloidal solutions are always neutral. But colloidal particles carry either +ve or −ve charge whereas the dispersion medium carries equal and opposite charges. Therefore, the system as a whole is electrically neutral.

Q. 3.36. What is a protective colloid ?

Ans. On adding a small quantity of a lyophilic sol to a lyophobic sol the later can be made more stable towards the precipitating action of electrolytes. The lyophilic sol used is known as protective colloid.

Q. 3.37 Name a substance which can form positive as well as negative colloids.

Ans. AgCl. When AgCl is present in a solution of $AgNO_3$, it attracts Ag^+ ions giving positively charged particle, whereas in a solution of KCl it attracts Cl^- ions giving negatively charged particles.

□ □

UNIT 4

Emulsions : Formation and the Role of Emulsifying Agents

4.1. INTRODUCTION

Colloidal state is not limited to dispersions of solid particles in a liquid medium ; it also includes the dispersions of liquids in liquids. Such dispersions are known as **emulsions**. Any two liquids which are immiscible with each other can form emulsions. For example, milk is an emulsion in which the particles of liquid fat are suspended in water. The dispersed phase is always in the form of small droplets. The droplets present in emulsions are some what larger than the suspended particles in sols.

Emulsions are of two types,

(*i*) **Oil-in-water type.** In such emulsions, the oil constitutes the dispersed phase whereas water is the dispersing phase. Milk and vanishing cream belong to this class of emulsions.

(*ii*) **Water-in-oil type.** In such emulsions, water is the dispersed phase whereas oil is the dispersing phase. Butter and cold creams are two common examples of this type of emulsion.

4.2. PREPARATION OF EMULSIONS AND THEIR STABILITY

The process of making an emulsion is known as **emulsification**. An emulsion may be prepared by shaking together two immiscible liquids vigorously. The process of agitating breaks one liquid into droplets of colloidal dimensions which in turn are dispersed through the body of the other liquid. The droplets of dispersed liquid tend to flocculate forming clusters of droplets which are too large to remain in the dispersed condition. As a result, the two liquids soon separate into two layers. Sometimes, a mixture of two liquids is subjected to ultrasonic vibrations. Emulsions are generally unstable. They may be stabilized by adding some emulsifying agent or emulsifier. These emulsifying agents decrease the surface tension of the two liquids, and thus, the tendency of the tiny droplets to coalesce and form aggregates is reduced.

The emulsifier forms a protective film at the oil-water interface and thus prevents breaking of the emulsion. Figure 4.1 shows the role of an emulsifying agent in stabilization of an emulsion. Most of the emulsifying agents contain both polar groups (*e.g.*, $-COO^-Na^+$, $-SO_3^-Na^+$) and non-polar groups (*e g.*, hydrocarbon chain). The non-polar end being hydrophobic dissolves in the oil and the polar end being hydrophilic dissolves in water.

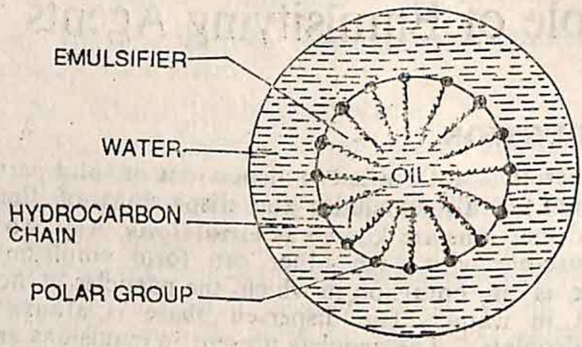


Fig. 4.1. Action of an emulsifier.

Soaps and detergents are the commonly employed emulsifying agents. Among other stabilizing agents include proteins, gum, agar, *etc*. The emulsifying properties of soaps and detergents have impact in washing of clothes and crockery. They owe their cleansing ability to the structures of their molecules which allow them to assume the role of emulsifying agents between dirt, grease or oil and water. The dispersed particles of soap adsorb (emulsify) fine particles of dirt and form a protective film about them. Thus, the dirt particles are held in suspension and are washed away.

Casein stabilizes milk, the oil-in-water emulsion.

Emulsification helps in the digestion of fats in the intestines. Intestines also contain some alkaline solution. A small amount of fat reacts with alkaline solution forming a sodium soap which emulsifies the remaining fat, and thus, digestive enzymes are helped by emulsification in carrying out their metabolic functions.

4.3. EXPERIMENTS

Experiment 4.1. To study and compare the effectiveness of a number of oils in forming emulsions.

Apparatus. 250 mL five stoppered bottles, 5 mL, 25 mL and 100 mL measuring cylinders, and a stop watch.

Chemicals. Coconut oil, ground nut oil, kerosene oil, mustard oil, castor oil, 1 per cent soap solution and distilled water.

General. All oils do not form emulsions with water with the sama ease as the ease of formation of emulsions depends upon the physical properties and chemical constitution of the oils.

Procedure. (*i*) Take five stoppered bottles and wash them thoroughly with distilled water followed by steam jet. Dry them in electric oven. Label these stoppered bottles as 1, 2, 3, 4 and 5.

(*ii*) Using a 25 mL measuring cylinder, measure out 10 mL of each of the five oily substances in five different bottles.

(*iii*) To each bottle, pour 100 mL distilled water with the help of the 100 ml measuring cylinder and 5 mL of 1% soap solution with the help of a measuring cylinder.

(*iv*) Stopper all the bottles tightly. Shake the contents vigrously say 40 shakes per bottle to ensure complete mixing.

(*v*) Observe the appearance of emulsions. Now allow these bottles to stand and record the time for breaking up of the emulsions in all the five bottles as suggested in Table 4·1.

Observations

Table 4.1

Bottle No.	*Oil*		*Volume of water* (mL)	*Volume of soap solution* (mL)	*Time taken for separation of two phases* (min)
	Name	*Volume* (mL)			
1	Coconut,	10	100	5	
2	Ground nut,	10	100	5	
3	Kerosene,	10	100	5	
4	Mustard,	10	100	5	
5	Castor,	10	100	5	

Result. The oil which takes the maximum time for separation from its emulsion is the most effective in forming emulsion.

Experiment 4.2. To study and compare the effectiveness of various emulsifying agents in imparting stability to an emulsion.

Apparatus. 100 mL four stoppared bottles, 5 mL and 50 mL measuring cylinders, stop watch.

Chemicals. Castor oil, 1.0 per cent solutions of each sodium oleate, sodium palnitate, gelatin and egg albumin, distilled water.

General. An emulsifier changes the interfacial tension between oil and water and gets trapped in the interfacial region. It makes a protective film round the droplets and prevents their coalescence, *i.e.*, stabilizes the emulsion. Different emulsifying agents, however, vary in their powers in lowering the interfacial tension between the dispersed phase and dispersion medium.

Procedure. (*i*) Wash the bottles thoroughly with water followed by steam jet. Dry them in an electric oven. Label these bottles as 1, 2, 3 and 4.

(*ii*) With measuring cylinders, pour 5 mL castor oil and 20 mL distilled water into each bottle.

(*iii*) Add 2 mL of 1.0 per cent sodium oleate solution to bottle no. 1. Shake the contents vigoursly for 2 min. Observe the formation of emulsion. Allow it stand.

(*iv*) Determine the time from the moment of rest to the moment the emulsion completely breaks, *i.e*, the separation of two layers (oil and water).

(*v*) Repeat the operation with the remaining three bottles by adding 1 mL of sodium palmitate, gelatin and egg albumin solutions to bottles 2, 3 and 4 respectively.

(*vi*) Tabulate the observations as suggested below.

Observations

Table 4.2

Bottle	*Volume of oil* (mL)	*Volume of water* (mL)	*Emulsifiers*		*Time taken far separation of two layers* (min)
			Name	*Volume* (mL)	
1	5.0	20.0	Sodium oleate	2.0	
2	5.0	20.0	Sodium palmitate	2.0	
3	5.0	20.0	Gelatin	2.0	
4	5.0	20.0	Egg albumin	2.0	

Result. The emulsifier, in the presence of which any emulsion takes maximum time to get separated into two layers, is considered to be the most effective in stabilizing the emulsion.

ORAL QUESTIONS AND ANSWERS

Q. 4.1. What is an emulsion ?

Ans. It is a type of colloidal system in which both the dispersed phase and the dispersion medium are immiscible liquids.

Q. 4.2, What are the different types of emulsions ?

Ans. Oil-in-water emulsions and water-in-oil emulsions.

An emulsion in which water forms the dispersion medium and oil droplets are dispersed is called an oil-in-water emulsion. An emulsion in which oil forms the dispersion medium and water droplets constitute the dispersed phase is called water-in-oil emulsion.

Q. 4.3. How will you detect the type of an emulsion ?

Ans. The following tests are employed :

(*a*) **Dye test** : Shake an oil-soluble dye with the emulsion under investigations. Then, take a drop of it and examine it under a microscope. If the drop is coloured, the emulsion is of oil-in-water type.

(*b*) **Spreading test.** Place a drop of an emulsion on an oil surface. If it spreads easily, the emulsion is water-in-oil type.

Q. 4.4. Classify the following emulsions into water-in-oil and oil-in-water type emulsions :

(*i*) milk, (*ii*) cold cream (*iii*) butter, (*iv*) vanishing cream, (*v*) mayonnaise.

Ans. Water-in-oil emulsion : butter, cold cream
Oil-in-water emulsion : Milk, vanishing cream mayonnoise.

Q. 4.5. Which of the two oil and water has greater surface tension in water-in-oil emulsions, and why ?

Ans. Water. Water has greater tendency to form spherical droplets and give water-in-oil emulsions.

Q. 4.6. What is emulsification ?

Ans. Emulsification is the process of producing emulsions.

Q. 4.7. What is an emulsifying agent or emulsifier ?

Ans. It is a substance which is added during emulsification to stabilize an emulsion.

Q. 4.8. Give some examples of emulsifying agents ?

Ans. Soaps, detergents, proteins, agar, gum, egg yolk, *etc*.

Q. 4.9. What would happen if emulsifying agents were not added in emulsions ?

Ans. In the absence of emulsifying agents, the dispersed droplets of the dispersed liquid will soon coalesce into larger globules and separate from the dispersing medium.

Q. 4.10. How does soap act as an emulsifier ?

Ans. A soap lowers the interfacial tension by orienting between water and oil. The non-polar chain of the soap molecule is attracted to the non-polar oil while the ionic head (hydro philic) is attracted to the water phase. The oil droplet thus becomes surrounded by an ionic layer which prevents their coalescence.

Q. 4.11. Comment on the role played by an emulsifier in the stability of emulsions ?

Ans. It forms a protective film around every drop of the dispersed phase and this prevents these drops from coalescence and consequent separation into two layers. It reduces the interfacial tension between the two immiscible liquids.

Q. 4.12. What is Bancroft rule ? State its uses ?

Ans. According to this rule, the phase in which the emulsifier (or stabilizer) is more soluble becomes the outer phase.

The rule is heepful in deciding the type of emulsion. For example, soaps, gelatin, *etc.*, which are insoluble in hydrocarbons but soluble in water give oil-in-water type emulsions. On the other hand, heavy metal soaps (*e.g.*, Ca. Al oleate) which are more souble in hydrocarbons than water yield water-in-oil type emulsions.

Q. 4.13. Comment Anlkali metal soap forms an oil-in-water type emulsion ?

Ans. An alkali metal soap, (*e.g.*, sodium oleate) causes lower interfacial tension at the water-soap film interface than at oil-soap film interface. The liquid, *e.g* , olive oil, whose interfacial tension with soap film is greater rolls into drops and produces an oil-in-water type emulsion.

Q. 4.14. Both calcium and magnesium oleate produce water-in-oil type emulsions comment ?

Ans. Calcium and magnesium oleates cause a lower interfacial tension at the oil-soap film interface and produce a water-in-oil type emulsion.

Q. 4 15. What type of emulsion is obtained by adding the following to a mixture of oil and water :

(*a*) Gelatin and (*b*) Aluminium oleate.

Ans. (*a*) Write in oil type (*b*) oil in water type.

Q. 4.16. Will you get an emulsion by mixing two miscible liquids ?

Ans. No, only a solution will be obtained.

Q. 4 17. What is demulsification ?

Ans It is a process of breaking an emulsion into two separate phases. This can be brought about by centifuging, boiling and freezing the emulsion. Electrostatic precipitation and certain chemical reaction are also helpful. All these devices destroy the emulsifying agent.

□ □

UNIT 5

Rate of Reaction : Effect of Concentration and Temperature

5.1. INTRODUCTION

The meaning of rate. It is faster to use the lift, slower to use the stairs The word fast and slow both describe the rate of going up or coming down. Rate is a measure of the 'change' that happens in a single unit of time. The unit of time can be a second, a minute or an hour. Many different rates of change are used in everyday life. A few examples are listed in Table 15.1.

Table 15.1. Some everyday experiences with rates of change

	Example	*Rate*
1.	Going to school by bus	30 kilometers per hour (kmph)
	Going to school by train	60 kilometers per hour (kmph)
2.	Playing a long playing (LP) record	30 revolutions of the turntable per minute (rpm)
	Playing a single	50 revolutions of turntable per minute (rpm)
3.	Pouring petrol from a hand operated pump	50 mL per second
	Pouring petrol from a electricity operated pump	500 mL per second

Rate of Chemical Change

In a chemical change, reactants change to products. Chemical reactions vary enormously in speed. Some proceed slowly over a period of months (*e.g.*, the rusting of iron) ; others take week to reach completion (*e.g.*, the fermentation of alcohol) ; some reactions are very fast (*e.g.*, neutralization of a strong acid and a strong base ; precipitation of insoluble salts) ; others are so fast as to be explosive (*e.g.*, the reaction between hydrogen and oxygen).

The speed of a reaction is called ite rate.

We have seen that different reactions occur with different speeds. In every reaction, the concentration of reactants decreases and the concentration of products increases with time. The speed at which a reaction takes place can be expressed as the **rate of reaction.** The rate of a chemical reaction is defined as the change in concentration of reactants or products per unit time.

$$\text{Rate of reaction} = \frac{\text{Change in concentration}}{\text{Time interval}}$$

$$= \frac{C_f - C_i}{\text{Time interval}} \qquad \text{...(5.1)}$$

here C_f and C_i are the final and initial concentations respectively (either reactant or product)

Now let us consider a simple reaction

$$R \dashrightarrow P$$

i.e., reactant, R, changes into product, P, the rate of this reaction can be calculated by substituting the concentration of either R or P at different interval times in the equation (5.1) on substituting these values in the equation 5.1, we get

$$\text{Rate} = \frac{[R]_f - [R]_i}{\text{Time interval}} = \frac{\Delta[R]}{\Delta t} \qquad \text{...(5.2)}$$

or

$$\text{Rate} = \frac{[P]_f - [P]_i}{\text{Time interval}} = \frac{\Delta[P]}{\Delta t} \qquad \text{...(5.3)}$$

On substituting the experimental values (the rate of reaction is always determined experimently) of the concentrations, we find that the rate as calculated from the equation 5.2 comes out to be negative. **The rate of a reaction is always positive.** Thus, whenever the rate is expressed in terms of the concentration of reactants, **a minus sign is always put before the expression.** This minus sign is because the concentration of the reactant decreases with time. Thus, the correct expressions for expressing the rate of a reaction are

$$\text{Rate} = -\frac{\Delta[\text{Reactant}]}{\Delta t}$$

or

$$\text{Rate} = +\frac{\Delta[\text{Product}]}{\Delta t}$$

If the concentration is expressed in moles per litre and the time in seconds, the units of rate work be in mol $l^{-1}s^{-1}$.

Measuring rates

The next important question is : how can amounts of reactants or products be measured ? This is often not easy to answer. In most of the reactions, reactants and products stay all mixed up, and in the same state.

In the reaction,

$$NaOH(aq)+HCl(aq) \longrightarrow NaCl(aq)+H_2O(l)$$

all the reactants and products are in the same state (or phase). This is called a homogeneous reaction.

To separate one of them and measure the amount of it can be difficult.

In this unit, we shall look only at reactions that give a products in a different state from the reactants. Because the product is in a different state (or differs in colour from the reactant, *etc.*) the amount of it can usually be measured easily.

Factors that affect rate of reaction

We have seen that reactions move with different speeds. The rate of a reaction depends upon the following factors:

(*i*) concentration, (*ii*) pressure, (*iii*) temperature, (*iv*) light, (*v*) surface area, and (*vi*) catalyst.

(*i*) An increase in the concentration of reactants produces an increase in the reaction rate. This holds true for most of the reactions.

(*ii*) As the concentration is a measure of the number of particles in a unit volume, an increase in pressure (particularly if the reactants are gases) leads to an increase in concentration. This in turn leads to an increase in the rate of reaction.

(*iii*) The reaction rate increases as the temperature increases. While the effect of concentration on rate is being studied, the temperature of the system is always held constant and *vice versa.*

(*iv*) Most of the reactions you perform in the laboratory are unaffected by light. Reactions that are speeded up by light are called photochemical reactions, *e.g.*, a mixture of hydrogen and chlorine gases explode when exposed to light. Photochemical reactions are not very common.

(*v*) The reaction rate increases when the surface area of the reactants is increased. Reaction of acid on powedered marble is much faster than on marble in chips form.

(*vi*) A catalyst, generally, increases the rate of a reaction, *e.g.*, synthesis of ammonia from N_2 and H_2 is catalyzed by iron.

Now we shall plan a few experiments for studying the effect of concentration and temperature on the rate of reaction.

5.2. EXPERIMENTS

Experiment 5.1. To study the effect of concentration of the rate of reaction between sodium thiosulphate and hydrochloric acid.

Apparatus. Beakers, conical flasks, burette, stop cock, measuring flasks, measuring cylinders.

Chemicals. Sodium thiosulphate, hydrochloric acid, distilled water.

General. The chemical reaction between sodium thiosulphate and hydrochloric acid is

$$Na_2S_2O_3(aq)+2HCl(aq) \longrightarrow 2NaCl(aq)+SO_2(g)+S(s)+H_2O(l)$$

or

$$S_2O_3^{2-}+2H^+ \longrightarrow SO_2+\underset{(ppt.)}{S}+H_2O$$

The rate of a chemical reaction is measured as the change of concentration of a reactant or product with time. Thus, for the reaction, one could measure the rate at which $Na_2S_2O_3$ or HCl is consumed or the rate at which colloidal sulphur is precipitated to form a milky white colloidal solution. However, the latter is a more convenient method.

From the rate expression, it follows that the higher the concentration of $S_2O_3^{2-}$ ions or H^+ ions or both, the higher will be the rate of formation of the products. Accordingly the rate of the reaction will decrease as the concentration of either $S_2O_3^{2-}$ or H^+ will decrease.

Procedure. (*a*) **Varying the concentration of sodium thiosulphate**

(*i*) Prepare 250 mL 1 M HCl solution by diluting ~22 mL conc. HCl to 250 mL in a measuring flask. The exact molarity can be known by titrating it against standard NaOH solution using phenolphthalein as indicator.

Using a burette, measure out 25 mL of dilute HCl in five beakers (100 mL). Put these beakers in a trough containing cold water.

(*ii*) Prepare 250 mL 0.5 M $Na_2S_2O_3$ solution (31.0 g/250 mL). Using a burette, measure out five different volumes say 25, 20, 1 , 10 and 5 ml of $Na_2S_2O_3$ solution in five conical flasks marked as 1, 2, 3, 4 and 5. Add distilled water in conical flasks marked 2, 3, 4 and 5 so that the total volume in each flask is the same. Put the flasks in a trough containing cold water. The concentration of each thiosulphate solution is now different.

(*iii*) Make a cross on a piece of paper, with a pencil.

Put the paper under the flask no. 1 containing the $Na_2S_2O_3$ solution, so that you can see the cross through the liquid.

(*iv*) Now pour the HCl solution into the $Na_2S_3O_3$ solution (flask no. 1). Start a stop clock at the same time. Swirl the solution in the flask.

(*v*) Determine the time from the moment of the addition of the HCl solution to the moment the cross completely disappears.

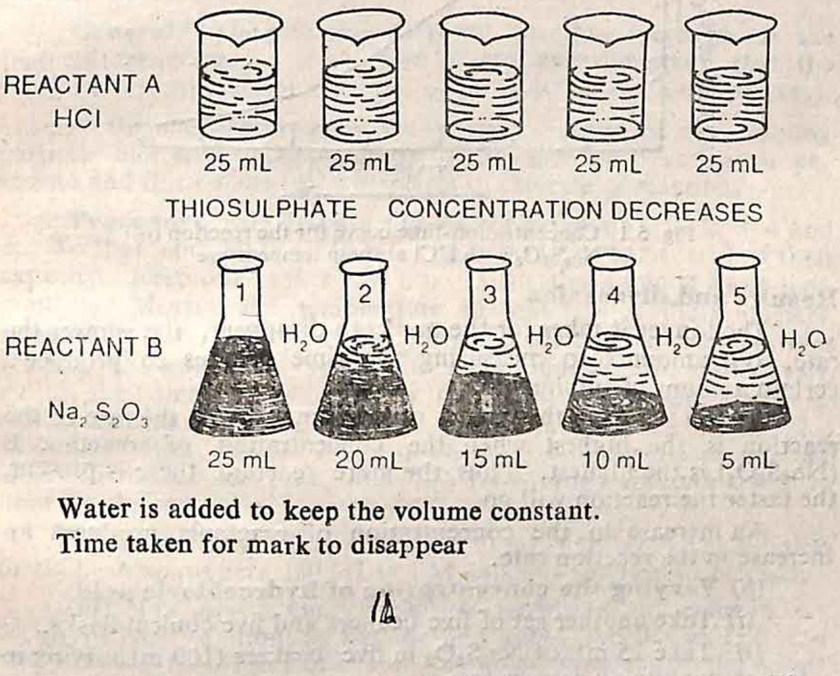
(*vi*) As the cloudy suspension forms, it blots out the cross from view. Stop the stop clock the moment the cross completely disappears.

(*vii*) Repeat the operation with the remaining four flasks.

(*viii*) Plot a graph of concentration of $Na_2S_2O_3$ solution (this is to be calculated, or just use the volumes of $Na_2S_2O_3$ solution used) against time. The shape of graph will be as given in Fig. 5.1.

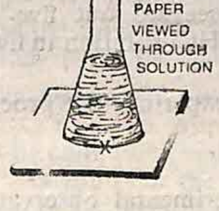
Experiment and observations

Acid concentration constant



Water is added to keep the volume constant.

Time taken for mark to disappear



Say

t_1	t_2	t_3	t_4	t_5
30s	37s	50s	75s	150s

it means rate decreases as the time consumed for the cross to disappear in flock 5 is maximum.

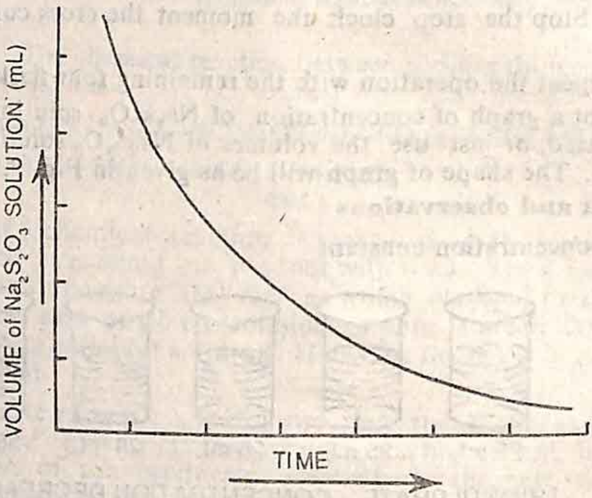


Fig. 5.1. Concentration-time curve for the reaction of $Na_2S_2O_3$ with HCl at room temperature.

Results and discussion

The longer it takes for the mark to disappear, the slower the rate, so it amounts to measuring the time it takes to produce a certain amount of sulphur.

As you see from the trend of the time taken the rate of the reaction is the highest when the concentration of reactant B ($Na_2S_2O_3$) is the highest. Thus, the more reactant there is present, the faster the reaction will go.

An increase in the concentration of reactants produces an increase in the reaction rate.

(*b*) **Varying the concentration of hydrochloric acid**

(*i*) Take another set of five beakers and five conical flasks.

(*ii*) Take 25 mL of $Na_2S_2O_3$ in five beakers (100 mL) lying in a trough containing cold water.

(*iii*) Using a burette, measure out five different volumes say 25, 20, 15, 10 and 5 mL of HCl solution in five conical flasks marked as 1, 2, 3, 4 and 5.

(*iv*) Now follow the experimental procedure as suggested in Experiment 5.1 (*a*).

Results and discussion

On the basis of experimental observations, you will observe that the rate of reaction increases with the increase in the concentration of H^+ ions, *i.e.* HCl.

Precautions. 1. Start the stop clock the moment mixing of two solutions is done.

2. View the cross mark through the reaction mixture from top.

Experiment 5.2. To study the effect of temperature on the rate of reaction between sodium thiosulphate and hydrochloric acid.

Apparatus. Beakers, burettes, thermometers, boiling tubes, stirrers, measuring flasks.

Chemicals. Sodium thiosulphate, hydrochloric acid and distilled water.

General. The rate of a chemical reaction increases as the temperature increases. It has been found experimentally that the rate of a typical reaction doubles for every 10°C rise in temperature.

As the temperature rises, the average speeds of the reacting particles increases. Consequently, there are more collisions per second and this results in an increases in the rate of reaction,

Procedure. (*i*) Prepare five water baths nos. 1, 2, 3, 4 and 5. To that end, fill five 250 mL beakers with water to $\frac{1}{2}$ of their capacity. Keep one beaker say no. 1. on the table at room temperature. Measure the temperature of water with thermometers. Heat water in remaining say 2, 3, 4 and 5 beakers to temperatures 5°, 10°, 15° and 20°C above the room temperature respectively. Adjust the flame of the burners so the water temperature remains almost constant (±0·5°C). Cover each beaker with a lid provided with four holes. Place a stirrer in one hole, a thermometer reading to 100°C in another hole, and the remaining rwo holes are to be used for the reactants.

(*ii*) In the mean time, prepare 250 mL 1 M aqueous solution of HCl. Also prepare 250 mL 0.5 M aqueous solution of $Na_2S_2O_3$.

(*iii*) Now using a burette measure out five equal volumes say 20 mL of HCl solution in five boiling tubes labelled as 1, 2, 3, 4 and 5. Insert tube no. 1 in one of the holes provided in the waterbath no. 1. Put the remaining tubes in the other waterbaths.

(*iv*) Pour 20 mL sodium thiosulphate solution into five different boiling tubes and put them in five different waterbarhs.

(*v*) Now take the waterbath no. 1 maintained at room temperature. Now add HCl solution from the boiling tube in water bath no. 1 to the test tube containing sodium thiosulphate solution in the same waterbath. As you pour the acid, start the stop clock. Mix the contents thoroughly and keep the tube on a cross mark on a white sheet of paper.

As the cloudy suspension forms, it blots out the cross from view (Experiments 5·1).

(*vi*) Stop the clock the moment the cross completely disappears. Determine the time that elapses from the moment when the HCl is added to the moment when the cross completely disappears.

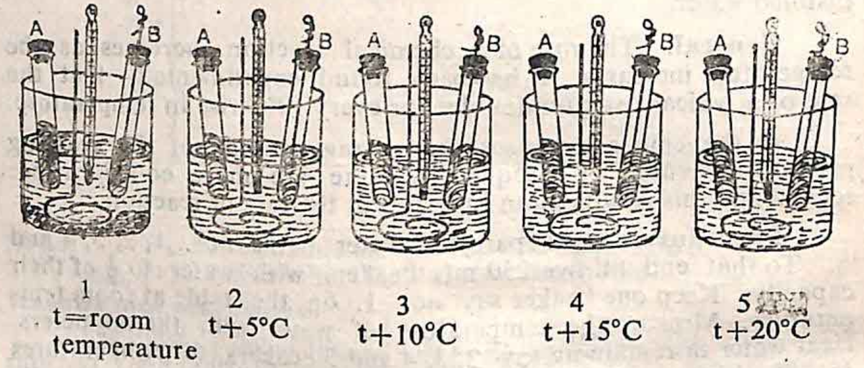
(*vii*) Now maintain the temperatures in different waterbaths as given below and repeat the operation in these waterbaths also. Determine the time of reaction as described for waterbath no. 1.

Experiment and observations

Reactants (constant concentration) (in water baths)

A—20 mL HCl solution

B—20 mL Na_2SO_3 solution



Increase in temperature ⟶ say

Time for mark to disappear	80 s	50 s	35 s	25 s

Increase in rate ⟶

Plot a graph between time in seconds and temperature.

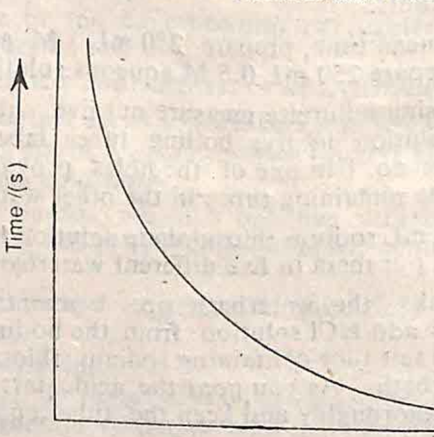


Fig. 5.2. Graph shows the change in time with change in temperature.

Results and discussion

From the observations and the graph you will see that the reaction rate increases as the temperature increases.

Note

(*i*) With the use of thermostat better results will be expected.

(*ii*) To determine the time for cross (drawn on a piece of paper as suggested in Experiment 5.1) to disappear accurately it is advised to carry out the reaction in a small conical flask, so that the visibility of cross is not hampered by the column of solution as in the case of boiling tube.

Precautions. Same as in Experiment 5.1.

ORAL QUESTIONS AND ANSWERS

Q. 5.1. What do you understand by the rate of reaction.

Ans. Refer to Section 5.1.

Q 5.2. What are the factors which could affect the rate of reaction ?

Ans. Refer to Section 5.1.

Q. 5.3. What are the homogeneous ond heterogeneous reactions ?

Ans. Homogeneous reactions are those in which the reactants and products are in the same phase. For example,

$$NaOH\ (aq) + HCl\ (aq) \longrightarrow NaCl\ (aq) + H_2O\ (l)$$

$$H_2\ (g) + Cl_2\ (g) \longrightarrow HCl\ (g)$$

Heterogeneous reactions are those in which the reactants and products are in different phases. For example,

$$2Mg\ (s) + O_2\ (g) \longrightarrow 2MgO\ (s)$$

$$Zn\ (s) + 2HCl\ (aq) \longrightarrow ZnCl_2\ (aq) + H_2\ (g)$$

Q. 5.4. What are the units of rate of a chemical reaction ?

Ans. Units of rate of a chemical reaction depends on how the concentration of the reactants are expressed. If the concentration is expressed in moles per litre and the time in seconds, then the units of reaction rate will be mol L^{-1} s^{-1}.

Q. 5.5. What is the order of a reaction ?

Ans. The order of a reaction is defined as the sum of the powers to which the concentration (or pressure) terms are raised in order to determine the rate of the reaction.

Q. 5.6. What is the differenee between molecularity and the order of a reaction ?

Ans. Molecularity of a reaction is the sum of the number of atoms, ions or molecules of reactants that take part in a chemical reaction as suggested through a balanced chemical equation.

The order of a reaction is given by the total number of atoms, ions, or molecules whose concentrations determine the rate or velocity of the reaction.

Q. 5.7. It is difficult to determine the rates of certain reactions. Comment.

Ans. Most of the ionic reactions are fast reactions. Explosive and combustion reactions are also considered to be fast reactions. For example, (*i*) burning of magnesium/phosphorus, (*ii*) neutralization of a strong acid and a strong base.

For slow reactions like rusting of iron and fermentation of alcohol, it is not easy to determine the rate.

Q. 5.8. How does the concentration of a reactant affect the rate of a reaction ?

Ans. The rate of reaction increases with the increase of concentration of the reactants.

As the concentration of molecules increases, the number of molecules in a unit volume also increases and hence the frequency of collision of the reacting molecules increases. Consequently the rate of a reaction increases.

Q. 5.9. What is the effect of temperature on the rate of reaction ?

Ans. It generally increases with the increase in temperature. However, sometimes, it may slow down the rate of reaction.

As the temperature rises, the average speeds of the reacting particles increase. Consequently, there are more collisions per second and this results in an increase in the rate of reaction.

Q. 5.10. Reactant particles do not always react when they collide. Comment.

Ans. During a chemical reaction, bonds are first broken and the new bonds are formed. Consequently, energy is required to break bonds and start this process. In case the energy available for the reaction is not sufficient the rearrangement of bonds may not take place, *i.e.*, reactant particles do not always react when they collide. A reaction occurs only as a result of those collisions between particles which possess more than a certain minimum amount of energy known as the activation energy.

□ □

UNIT 6

Paper Chromatography

6.1. INTRODUCTION

Chromatography (chroma, Latin word means colour and graphy means separation) is a means of separating mixture by distribution of the components between stationary phase and a mobile phase. The stationary phase is a solvent (often water) adsorbed (bonded to the surface on a solid). This may be paper or a solid such as alumina or silica gel, which has been packed into a column or spread on a glass plate. The mobile phase is a second solvent which moves slowly through the stationary phase.

The chromatographic separations can be achieved by the **adsorption or partition mechanisms.** In **adsorption chromatography** the components of a mixture are separated by their different adsorption/desorption natures in the presence of a mobile phase. This is because the substances possess differing affinities with the mobile phase and varying interactions with the surface of the solid (stationary phase).

Absorption chromatography is classified on the basis of mobile phase used, *i.e.* liquid/solid or gas/solid.

Partition chromatography involves the distribution of the components of a mixture between a liquid adsorbed on a solid and a mobile solvent.

A number of techniques employing the basic principles of chromatography have been developed and are described in Table 6.1.

Table 6.1. Different types of techniques of chromatography

Description	*Stationary phase*	*Mobile phase*	*Principle involved*	*Use*
Paper	Adsorbed water on paper	Liquid	Partition cum-adsorption	Identification
Column	Adsorbed water (or solvent) on silica gel or alumina	Liquid	Adsorption	Purification and separation of compounds
Thin layer	Adsorbed water (or solvent)	Liquid	Adsorption	Identification and separation of components
Gas-liquid	Non-volatile solvent adsorbed on powder	Insert gas like N_2 or He	Partition	Identification
Gas-solid	Surface of powder	Inert gas	Partition	Identification
Ion-exchange	Ionic sites on resins	Aqueous reagents	Partition	Softening of hard water.

6.2. PAPER CHROMATOGRAPHY

In paper chromatography, as stated earlier, the stationary phase is water adsorbed on the paper (cellulose). The mobile phase known as the **developing solvent or irrigant** is either a pure solvent or a mixture of solvents. At times it is also called **eluent.**

The mobile phase moves by capillary action through the body of paper. Three types of paper chromatography have been developed :

(*i*) **Ascending paper chromatography.** The mobile phase moves up across paper strip in this case.

(*ii*) **Descending paper chromatography.** The mobile phase descends across the paper strip.

(*iii*) **Circular paper chromatography or Radial chromatography.** The mobile phase moves horizontally along a circular sheet of paper.

A solution of the mixture (called test solution) to be separated is applied to a strip of chromatography and dried. Size of the strip depends upon the size of glass jar and number of spots to be applied. This is hung in a glass jar so that the ends dip into developing solvent in the bottom of the tank (Fig. 6.1). As the

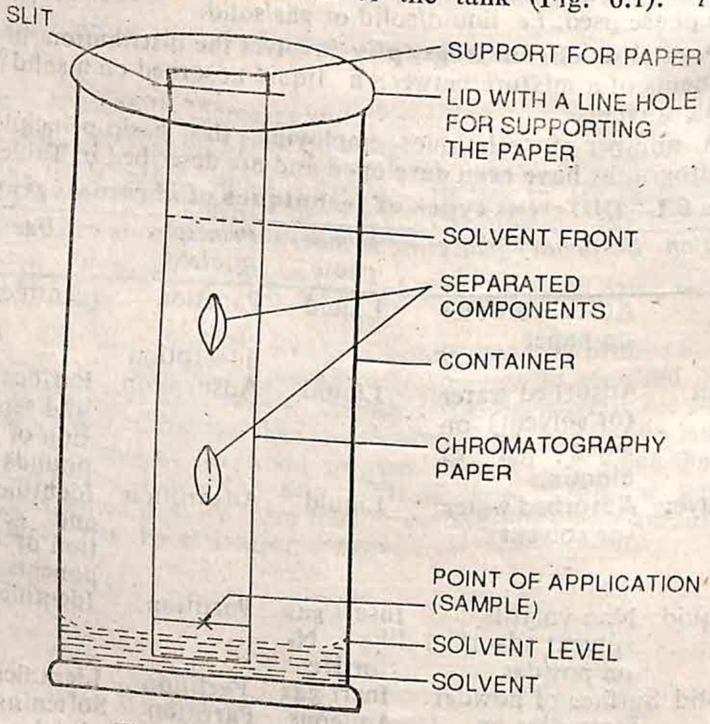


Fig. 6.1. Ascending paper chromatography

solvent moves up across the paper, it meets the test sample. As it rises across the paper, it separates the components. The glass jar is covered so that the atmosphere is saturated with solvent. If it is not covered, the solvent also evaporates from the paper. After the solvent has traversed ~75% of the length of the paper, the paper is removed from the container and dried.

Now at this stage, if the substances being separated are coloured, then detection of the spots of the components on the chromatogram is visible to the naked eye. In the case of colourless substances, they have to be spotted by spraying a developer which can form their coloured derivatives or some kind of complex, *etc.* The developer is sprayed with the help of a sprayer (Fig. 6.2).

Now dry the chromatograms either at room temperature or as advised by the teachers. Once the chromatogram is ready the distance travelled by the solvent front is measured. Each component of the test solution moves a characteristic distance relative to the solvent front. This distance is known as the R_f value (R_f=retention factor) and is defined as **the ratio of the distance travelled by the solute from the origin line to the distance travelled by the solvent from the origin line**, *i.e.*

$$R_f = \frac{\text{Distance travelled by the solute from the origin line}}{\text{Distance travelled by the solvent from the origin line}}$$

Pictorial respresentation of R_f has been made in Fig. 6.3 in which the solute has moved through a distance A from its point of application, *i.e.* the origin, whereas the solvent has moved through a distance B from the origin. Hence, in this case $R_f = A/B$.

The R_f value is dependent on the substance, solvent, paper and temperature. The different components are most reliably identified by running reference samples under the same conditions (Fig. 6.4). The reference samples contain the possible components of the mixture. So a chromatogram is developed using a sample of the mixture, and the samples of the possible components of the mixture. The positions of the spots from the spots of reference samples are compared. Thus R_f value can be used to assist in identifying the components of a mixture.

In **descending paper chromatography,** a chromatography tank with a trough near the top of the tank to hold the solvent is used. The paper hangs down from this trough and solvent descends across the paper (Fig. 6.5).

In **radial paper chromatography (or circular paper chromatography)**, a circular filter paper is taken. A hole is made in the centre of paper and a cotton wick is inserted into the hole. Spots of the materials to be analyzed are placed at the centre of the circular filter paper away from the fine end of the wick. The paper is positioned horizontally on the petridish containing the solvent so

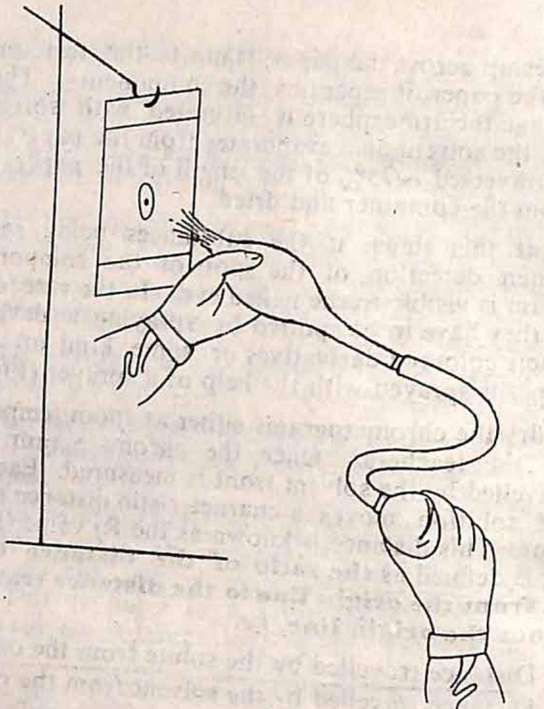


Fig. 6.2. Spraying of the chromatogram

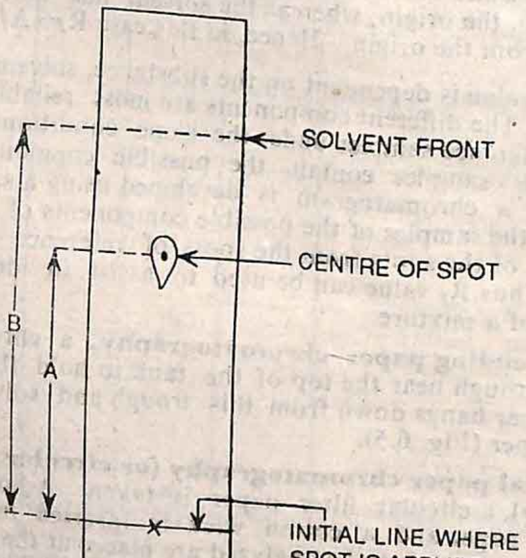


Fig. 6.3. Pictorial representation of $R_f : R_f = \frac{A}{B}$

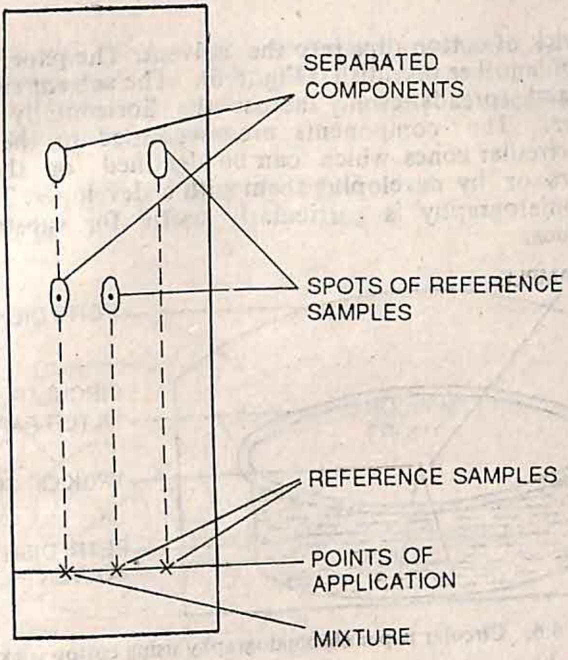


Fig. 6.4. Comparison of the spots of separated components with the spots of reference samples.

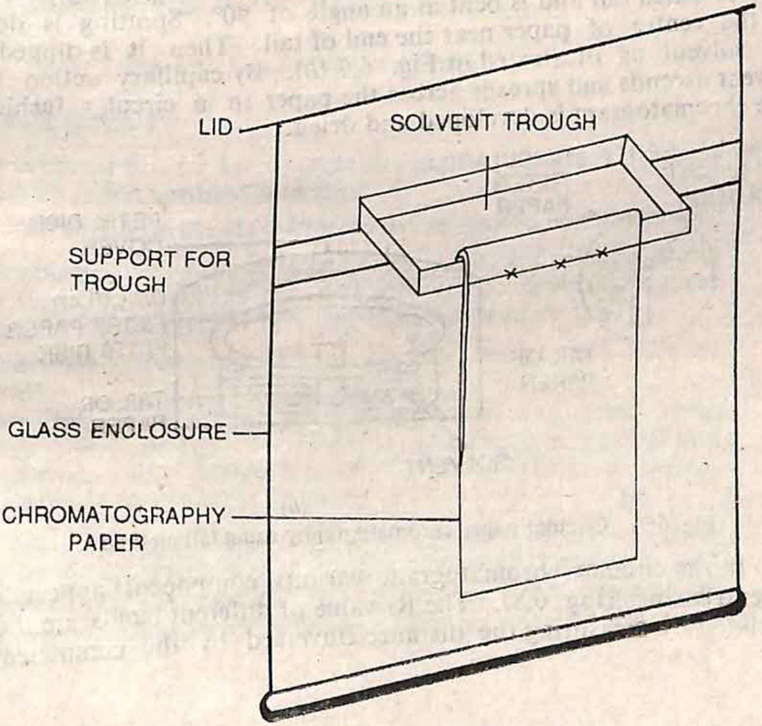


Fig. 6.5. Descending paper chromatography

that the wick of cotton dips into the solvent. The paper is covered by means of another petridish (Fig. 6.6). The solvent rises through the wick and spreads evenly across the horizontally positioned filter paper. The components are separated in the form of concentric circular zones which can be identified on the basis of their colours or by developing them with a developer. This type of paper chromatography is particularly useful for substanccs with low R_f values.

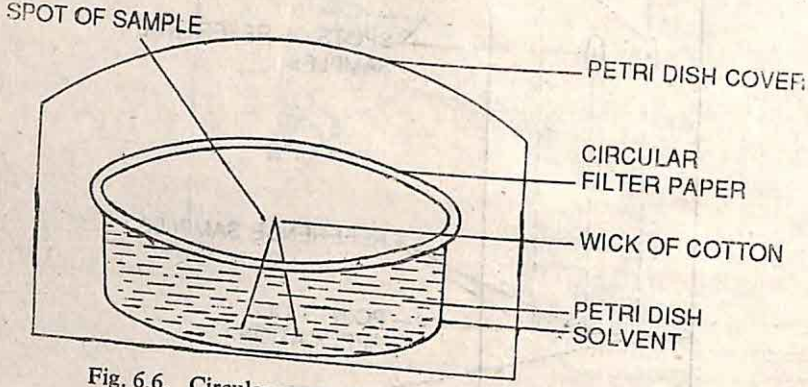
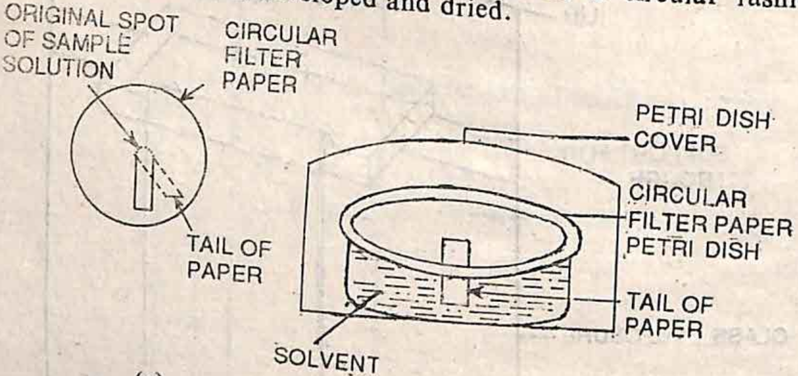


Fig. 6.6. Circular paper chromatography using cotton wick

In another method, a small strip of the paper is cut along the radius of the circular filter paper as shown in Fig. 6.7 (*a*)]. This strip is called tail and is bent at an angle of 90°. Spotting is done at the centre of paper near the end of tail. Then it is dipped in the solvent as illustrated in Fig. 6.7 (*b*). By capillary action the solvent ascends and spreads across the paper in a circular fashion. The chromatogram is developed and dried.



(*a*) (*b*)

Fig. 6·7. Circular paper chromatography using tail method

In the circular chromatogram various components appear in concentric rings (Fig. 6.8). The R_f value of different bands are then calculated by measuring the distance traversed by the components and the solvent from the central spot. At times the distance travelled both by the solvent and the components is different at different points along the bands. In such cases, the R_f is calculated at different points and average is taken.

$$\text{Mean } R_f = \frac{\frac{OA}{OA'} + \frac{OB}{OB'} + \frac{OC}{OC'} + \frac{OD}{OD'}}{4}$$

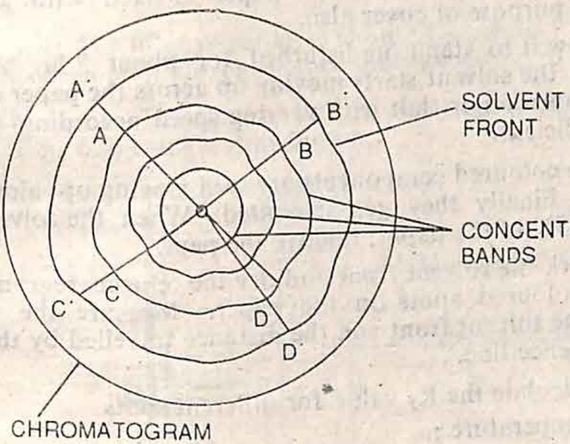


Fig. 6.8. Circular chromatogram.

6.3. EXPERIMENTS

Experiment 6.1. (*i*) To separate the pigments present in leaves and flowers by paper chromatography.

(*ii*) To determine the R_f values of the separated components.

Apparatus. Whatman filter paper sheet no. 1, a glass cylinder or jar, jar cover with a line whole, a capillary tube, drier (air blower or electric drier) pencil, scale, *etc.*, pestle and mortar, *etc.*

Chemicals. Acetone, alcohol, distilled water and flowers/leaves/petals.

Procedure. (*i*) Take some flowers/leaves and grind them into a mortar using pestle. Add 2-3 mL of acetone or alcohol and again grind them well. Collect the extract (or solution) by decantation or filtration in test tube and cork it.

(*ii*) Cut out a filter paper strip of size 5 cm × 30 cm (depends upon the size of the jar). Draw a horizontal line with a lead pencil at a distance of ~3 cm from one of the ends of the filter paper. This is called the reference or initial line.

(*iii*) Put a pencil mark in the middle of the reference line. Now by using a fine capillary put 2 or 3 drops of the extract stored in a test tube on the mark. Dry it using a blower or drier. Put two more drops at the same point and again dry it.

(*iv*) Take ~ 40 mL of the developer (acetone or alcohol) so as to give ~ 3 to 4 cm column of the liquid into the glass cylinder. Now hang the filter paper as shown in Fig. 6.1 so as the reference line is above the surface of the developing solvent. The lid or cover with a slit in which the paper is fixed with gum *etc.* will serve the purpose of cover also.

(*v*) Allow it to stand undisturbed for about 2 hr. You will observe that the solvent starts moving up across the paper carrying the constituents alongwith it with varying speed according to their partition coefficient.

(*vi*) The coloured components are seen moving up along with the solvent. Finally they get separated. When the solvent front traverses ~ 75% of the papar, remove the paper.

(*vii*) Mark the solvent front and dry the chromatogram. Now encircle the coloured spots on the paper. Measure the distance travelled by the solvent front and the distance travelled by the spots from the reference line.

(*viii*) Calculate the R_f value*for different spots

Temperature :...

Observations :

Distance of spot A from the reference line =X cm

Distance of the spot B from the reference line =Y cm

Distance of the solvent front from the reference line =Z cm

Calculations : R_f of spot, A $A=\frac{X}{Z}$

R_f of spot, B $B=\frac{Y}{Z}$

Result. The R_f values of the spots A and are.... ......respectively.

Precautions. (*i*) The spot of the sample solution on the reference line should be as small as possible; large spots give very diffuse spots after separation. Whilings, spotting, drying, of the spot is important.

(*ii*) To get small spot, a fine capillary should be used.

(*iii*) Filter paper should not touch the side walls of the cylinder.

(*iv*) Reference line should always be ~ 1 cm above the surface of the developing solution.

(*v*) Paper should not come in the contact of bottom of cylinder.

(*vi*) Mark the solvent front the moment the paper is taken out of the cylinder.

(*vii*) Don't disturb the cylinder during the course of experiment.

(*viii*) The filter paper strip should be exposed to the vapours of the developing solvent before putting in use to get good results.

Note : 1. The experiment can also be carried out in a boiling tube (Fig. 6.9) using a drawing pin.

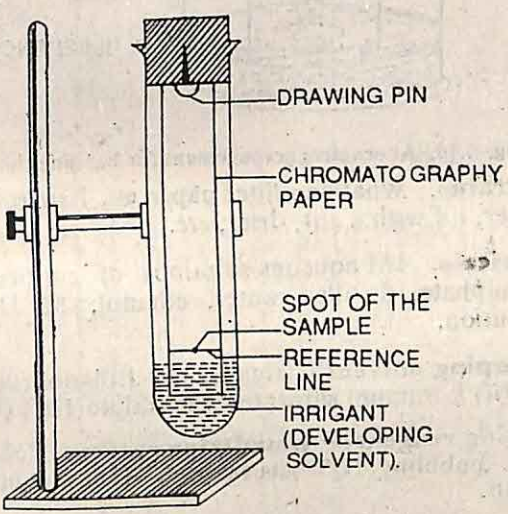


Fig. 6.9. A simple apparatus for ascending paper chromatography

2. If the lid with a line slit is not available hang the paper with the help of a glass rod and paper clips (Fig. 6.10).

3. A mixture of blue and red inks using alcohol (developing solvent) can also be separated on the lines suggested in the Experiment 6.1 by using alcohol as mobile phase.

4. The separation of coloured constituents present in a mixture can also be done by using circular paper chromatography. Coloured constituents separate as concentric rings.

Experiment 6.2. To separate Cu^{2+} and Cd^{2+} ions present in a given mixture using paper chromatography.

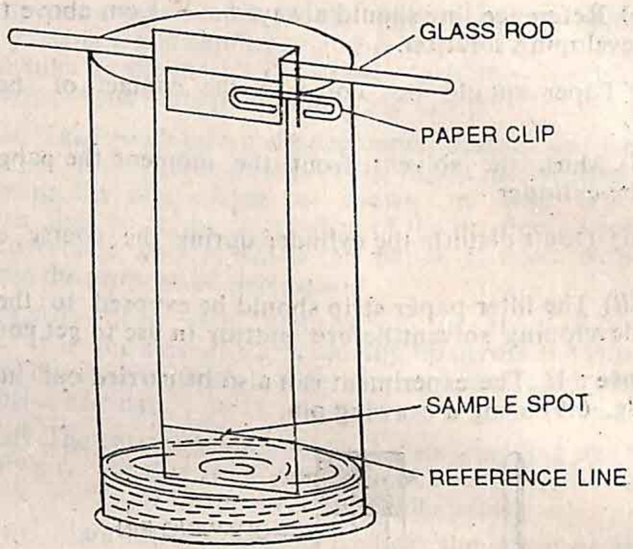


Fig. 6.10. Alternative arrangement for hanging the paper

Apparatus. Whatman filter paper no. 1 strip, capillary tube, glass cylinder, lid with a slit, drier, *etc.*

Chemicals. 1M aqueous solutions of copper sulphate and cadmium sulphate, distilled water, ethanol, 5N HCl, colourless $(NH_4)_2S$ solution.

Developing solvent (Irrigant). (*i*) Ethanol (90 mL)+5NHCl (10 mL) or (*ii*) *n*-Butanol saturated with dilute HCl (4N).

Spraying reagent or visualizing reagent. Colourless $(NH_4)_2S$ prepared by bubbling H_2S gas through dilute aqueous ammonia (4N) solution.

Procedure. (*i*) Take a Whatman filter paper no. 1 strip according to the size of the glass cylinder. Draw the reference line near the end of the strip at least above 3 cm from the edge of the strip. Mark three points on the reference line with proper spacing.

(*ii*) Apply a spot of each, 1M aqueous solution of copper sulphate, cadmium sulphate and a mixture of copper sulphate and cadmium sulphate against marks 1, 2, 3. Allow the spots to dry.

(*iii*) Pour the developing solvent (*i.e.*, mobile phase), a mixture of ethanol and HCl (9 : 1) so that it gives a column of 3 cm height.

(*iv*) Hang the paper in the cylinder as suggested earlier in the Experiment 6.1.

(*v*) Allow the mobile phase to move across the paper for at least 2 hr. or until it moves up 75% of the length of the paper strip.

(*vi*) Remove the paper strip and mark the solvent front.

(*vii*) Dry the paper strip and then spray colourless $(NH_4)_2S$ solution.

(*viii*) Note the colour and positions of spots. Identify each ion from the colours and calculate their R*f* values.

Observations

1. Black spot originating from mark 1 corresponds to Cu^{2+}.
2. Yellow spot originating form mark 2, corresponds to Cd^{2+}.

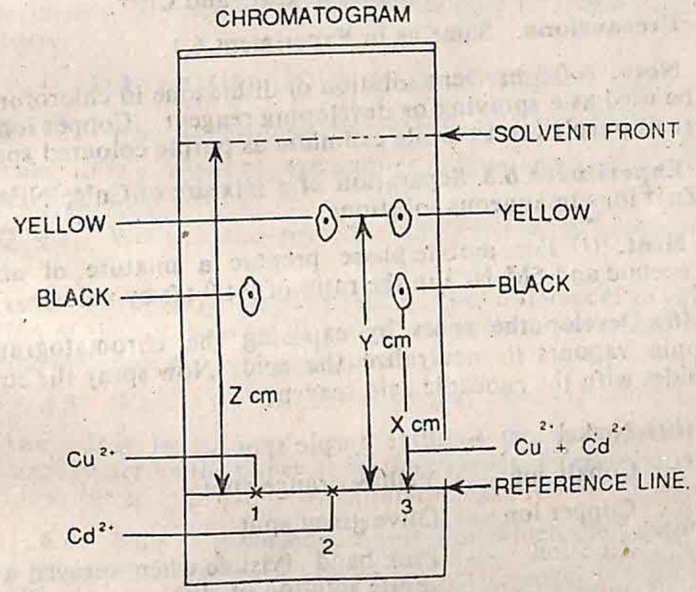


Fig. 6.11

3. Black spot originating from mark 3 well compares with the block spot originating from mark 1. Both the spots are almost at the same distance from reference line. Hence both the spots are because of CuS.

Yellow spots can also be similarly explained. They are because of CdS.

Calculations

Distance between the reference line and the centre of the black developed spot originating from mark 3=X cm.

Distance between the reference line and the centre of the yellow developed spot originating from mark 3 =Y cm.

Distance between the reference line and the solvent front =Z cm

R_f of black spot (Cu^{2+} S^{2-}) $= \frac{X}{Z}$

R_f of yellow spot (Cd^{2+} S^{2-}) $= \frac{Y}{Z}$

Result. R_f values of Cu^{2+} and Cd^{2+} have been found to be in the order, *i.e.* $Cd^{2-} > Cu^{2+}$ and they are in agreement with the values obtained from the known samples of Cu^{2+} and Cd^{2+}.

Precautions. Same as in Experiment 6.1.

Note. A 0.5 per cent solution of dithiazone in chloroform can also be used as a spraying or developing reagent. Copper ions will appear as purple brown while cadmium as purple coloured spots.

Experiment 6.3. Separation of a mixture of Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} ions in aqueous solutions.

Hint. (*i*) For mobile phase prepare a mixture of acetone, ethyl acetate and 5M HCl in the ratio of 9 : 9 : 2 by volume.

(*ii*) Develop the spots by exposing the chromatogram to ammonia vapours to neutralize the acid. Now spray the strip on both sides with the rubeanic acid reagent.

(*iii*) Nickel ion — Blue purple spot
Cobalt ion — Yellow orange spot
Copper ion — Olive green spot
Zinc ion — Pink band (visible when sprayed with a dilute solution of dithiazone in $CHCl_3$)

Experiment 6.4. Separation of a mixture of Pb^{2+} (aq), Ag^+ (aq) and Hg_2^{2+} (aq) ions.

Hint. (*i*) For mobile phase use distilled water.

(*ii*) Develop the spots by spraying 0.25 M potassium chromate solution.

(*iii*) Pb^{2+}	Yellow spot
Ag^+	Brick red spot
Hg_2^{2+}	Orange spot

Experiment 6.5. Separation of a mixture of Fe^{3+} (aq) and Al^{3+} (aq) ions.

Hint. (*i*) For mobile phase prepare a mixture of ethanol, isopropanol and dilute HCl in the ratio of 9 : 9 : 2.

(*ii*) Use a 1.0 per cent solution of alizarin in ethanol as spraying reagent. Expose the chromatogram to ammonia vapours.

(*iii*) Al^{3+}	Red spot
Fe^{3+}	Purple spot.

Now after seeking the instructions from the class teacher, other separations can be planned on the lines of Experiment 6.2. Planning of experiments depends upon the availability of reagents in your laboratory.

ORAL QUESTIONS AND ANSWERS

Q. 6.1. What is chromatography ?

Ans. It is a means of separating the components of a mixture and purifying components.

Q. 6.2. What is the principle underlying chromatographic process ?

Ans. Chromatography is based on the differences in rates of migration of the components of a mixture across a stationary phase under the influence of the moving phase.

Q. 6.3. What is the principle of paper chromography ?

Ans. It is based upon the fact that the components of a mixture move across the paper at varying speeds as the developer is sucked into the strip of paper by capillary action.

Q. 6.4. Name the basic mechanism on which the chromatographic separations are based.

Ans. Chromatographic separations can be achieved by the adsorption or partition mechanism.

For more information refer to Section 6.1.

Q. 6.5. What do you understand by the term 'R_f value' ?

Ans. R_f or 'retention factor' of a substance is the ratio of the distance travelled by the solute from the reference line to the distance travelled by the solvent from the reference line.

i.e.
$$R_f = \frac{\text{Distance moved by the component}}{\text{Distance moved by the solvent front}}$$

The R_f value is dependent on the substance, solvent, paper and temperature. It is independent of the length of the paper. It is never more than unity.

Q. 6.6. What are the moving (or mobile) and stationary phases in paper chromatography ?

Ans. Water adsorbed by paper acts as a stationary phase whereas the mobile liquid or the developing solvent acts as a mobile phase.

Q 6.7. What is a chromatogram ?

Ans. A filter paper used as adsorbent in paper chromatography when passes through the various stages of chromatography technique to the stage of spraying and drying is called chromatogram.

Q. 6.8. What are visualization reagents ?

Ans. When the substances being separated are coloured, then their positions are detected easily on the chromatogram. However, if the substances are colourless, they are not visible on the chromatogram. Their presence can be detected by applying some regents called visualization reagents.

Q. 6.9. What is development ?

Ans. The process of allowing the substance to move across the filter paper strip (stationary phase) under the influence of mobile phase is called development.

Q. 6.10. What is resolution ?

Ans. It is the degree of separation of the components of a sample after development on a chromatogram.

Q. 6.11. What typss of solvents are generally employed in chromatography ?

Ans. To achieve effective separations, solvents with low viscosities are generally employed because the rate of flow of solvent is inversely proportional to the viscosity.

Q. 6.12. Give the difference between one-dimensional and two-dimensional paper chromatography.

Ans. When the flow of liquid across the filter paper takes place in one direction, it is called one-dimensional chromatography. In two-dimensional chromatography, the liquid flows across the filter paper in two directions at right angles to each other.

Q. 6.13. What happens if the filter paper strip touches the side walls of the glass cylinder ?

Ans. The mobile phase moves unevenly and the separation of the components of a sample is not effective.

Q. 6.14. It is advised to cover the container when the chromatographic separation is on. Comment.

Ans. The container is covered so that the atmosphere is saturated with solvent and to prevent the evaporation of the solvent from the paper.

Q. 6.15. Is chromatography is useful for separating amino acids and sugar ?

Ans. Yes.

Q. 6.16. List some of the important biochemical applications of chromatography.

Ans. It is used in separating amino acids, proteins, sugars, nucleic acids, *etc*.

Q. 6.17. What is the basic difference between paper and column chromatographies ?

Ans. Paper chromatography is fast, but it is only suitable as a means of qualitative analysis. Column chromatography is used for the quantitative separation of mixtures.

Q. 6.18. What is advantage of descending paper chromatography over ascending paper chromatography ?

Ans. The main advantage of the descending paper chromatography is that the solvent can be allowed to flow off the paper if it is desired to elute the separated components.

Q. 6.19. Is it possible to separate the isotopes of an elements by chromatographic means ? Give reason for your answer.

Aus. No. Differences in chemical properties of the components of the sample are the basis of chromatographic separations, and since isotopes have same chemical properties, they cannot be separated by this technique.

□ □

UNIT 7

Volumetric (Titrimetric) Analysis

7.1. INTRODUCTION

Volumetric (Titrimetric) analysis is the quantitative determination of the components of a mixture by allowing to react the measured volumes of two solutions so that the reaction is just complete. In volumetric analysis, one solution of known concentration is used. This is termed as the **volumetric standard**. One of the two solutions is taken with a measuring device known as a burette. This could be a standard solution ; it is then gradually added to the solution (kept in a titration flask) to be analysed until the reaction is complete. This operation is known as titration. The progress of a reaction is followed by an indicator ; the indicator is used to determine the completion of a reaction (stoichiometric point) usually by a colour change. The correctness of volumetric results depends upon the measuring vessels, measurement of volumes and weighing.

Volumetric analysis has certain advantages over the other methods of quantitative analysis, such as gravimetric analysis. These are :

1. Volumetric analysis does not involve laborious and tedious operations, such as precipitation, filtration, washing, drying and ignition.
2. Volumetric determinations are more rapid and accurate.

Based upon the nature of chemical reactions various classes of volumetric analysis have been recognized.

—Acidimetry and alkalimetry

—Redox titrations

—Titrations involving precipitations reactions

—Complexometric titrations.

7.2. REQUIREMENTS FOR REACTIONS USED IN VOLUMETRIC ANALYSIS

The point in a titration when the amount of titrant added is the stoichiometric amount needed to react with the measured amount of the other reagent is called the **equivalence point** (end point), the point at which the colour change of the indicator becomes apparent to the eye. It is, therefore, obivous that it is necessary in titration to determine the equivalence point with sufficient accuracy. It is on this point that calculation of results is based. Thus the end point of titration is the point at which the indicator shows the reaction to be complete. At times, there is a difference between the stoichiometric and practical end point. This difference is termed as **titration error**. The choice of indicator should be such that the titration error is as small as possible by controlling the experimental conditions.

It is essential in a titration that at least one solution is of exactly known concentration (volumetric standard). Its concentration may be determined from another titration, but there must be a substance in the analytical procedure which is a **primary standard**. A primary standard is a substance which can be converted into a standard solution by weighing the material accurately on an analytical balance and dissolving it in water to obtain a solution of exactly known volume. To qualify as a primary standard, the substance must be pure, *etc*. (Unit I). Typical primary standards are anhydrons sodium carbonate, oxalic acid, Mohr's salt, *etc*.

Estimation by volumetric analysis is feasible only if the reaction involved fulfills the following conditions :

(*i*) The reaction must take place till completion and instantaneously.

(*ii*) The end point should coincide with the equivalence point.

(*iii*) There should be no side reactions.

(*iv*) The reaction should be specific.

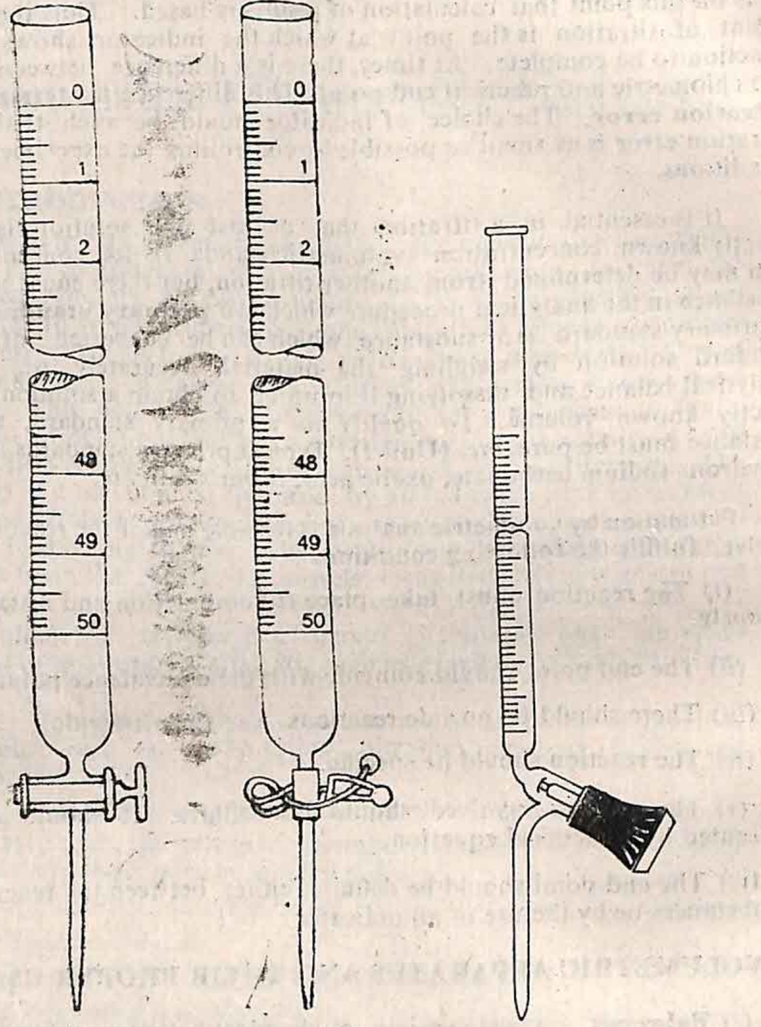
(*v*) The reaction involved should be definite. It should be represented by a chemical equation.

(*vi*) The end point should be definite, either between the reacting substances or by the use of an indicator.

7.3. VOLUMETRIC APPARATUS AND THEIR PROPER USE

(*i*) **Balances**. A wide variety of chemical balances is available each with its own operating procedure. It is important that the balance be kept clean. Spillages should not occur. Materials should not be added to, or removed from, the balance while the lever is free to move ; it must be arrested first. Methods for weighing the material have been discussed in Unit 1.

(*ii*) **Burettes**. Burettes commonly used in the laboratories are graduated from 0 to 50 mL and every division can read up to 0.1 mL. These are of various types (Fig. 7·1).



(a) Burette with Stopcock (b) Burette with Pinchcock (c) Burette with side screw

Fig. 7.1. Types of burettes.

Rinse the burette with the solution and ensure that it runs freely and is not blocked by dirt or grease.

Filling of burette and taking of the reading are two important steps.

Filling of burette

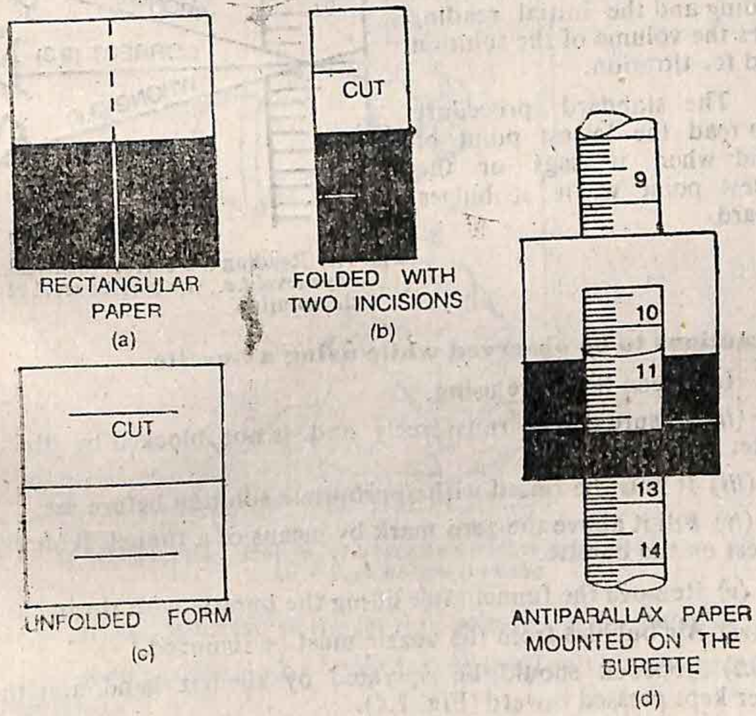
(*i*) Clamp the burette vertically in a burette stand.

(*ii*) Close the stopcock and pour the appropriate solution into the burette through a funnel (rinsed with the solution to be poured into the burette), held in left hand at its mouth to provide space for air to go out.

(*iii*) Run the burette until the meniscus is on or just below the zero mark.

(*iv*) Remove the funnel and allow it to stand for a minute or two so that the solution adhering to the upper part of the burette drips down.

(*v*) Check up that there are no air bubbles either in the tube or nozzle of the burette. In case there are any air bubbles, open the stopcock for the solution to flow quickly. The air bubble will escape quickly.



RECTANGULAR PAPER (a)

FOLDED WITH TWO INCISIONS (b)

UNFOLDED FORM (c)

ANTIPARALLAX PAPER MOUNTED ON THE BURETTE (d)

Fig. 7.2 (*a*, *b*, *c*, *d*) Anti-parallax paper index ; correct method of reading the liquid level.

Taking the burette reading

This involves the following steps :

(*i*) **Removal of parallax.** It is done with the help of anti-parallax paper index and is prepared by folding a rectangular piece of white paper into two halves and then giving to it incisions at two places [Fig. 7.2 (*a* and *b*)]. Now open the fold and mount the paper index on the burette [Fig. 7.2 (*c*) and (*d*)].

(*ii*) **Reading the correct meniscus.** Anti-parallax paper index is allowed to slip over the burette and is finally held against the level of the solution. Keep your eye in level with the lower meniscus of the solution and the black boundary, and note the initial reading of the burette as shown in Fig. 7.3. Similarly note down the final reading of the burette. The difference between the final reading and the initial reading gives the volume of the solution used for titration.

The standard procedure is to read the lowest point of liquid when it sags or the highest point when it bulges upward.

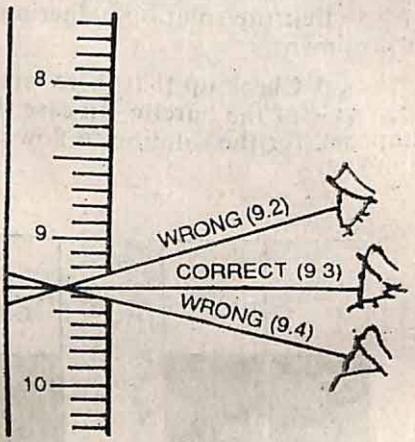


Fig. 7.3. Reading the correct meniscus at eye level *i.e.*, the correct level of the solution.

Precautions to be observed while using a burette

(*i*) Clean it before using.

(*ii*) Ensure that it runs freely and is not blocked by dirt or grease.

(*iii*) It must be rinsed with appropriate solution before use.

(*iv*) Fill it above the zero mark by means of a funnel. It should not rest on the burette.

(*v*) Remove the funnel after filling the burette with titrant.

(*vi*) Air bubbles from the nozzle must be removed.

(*vii*) Stopcock should be operated by the left hand and the stopper kept pressed inward (Fig. 7.4).

(*viii*) Always use anti-parallax paper index when taking a reading. It facilitates reading.

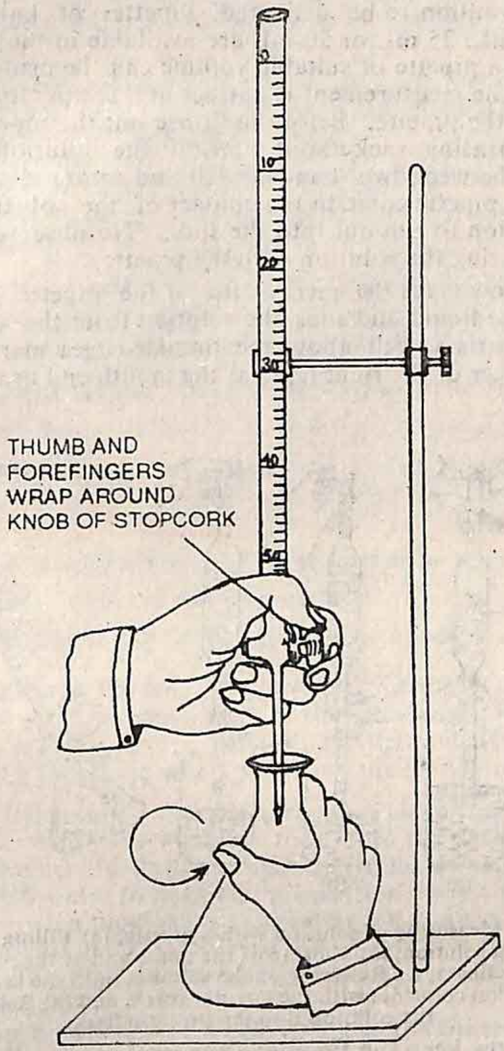


Fig. 7·4. **Holding the burette stopcock and the conical flask during titration.**

(*ix*) Adjust your eye at the level of solution in the burette.

(*x*) Reading should be recorded immediately in the practical record book.

(*xi*) After completing the titration, the burette should be thoroughly washed with water.

(*iii*) **Pipettes.** These are also measuring vessel to measure the volume of solution to be delivered. Pipettes of known volume say 10 mL, 20 mL, 25 mL or 50 mL are available in the market and the selection of a pipette of suitable volume can be made at the time of titration. The measurement is correct at a temperature engraved on the bulb of the pipette. Before use rinse out the pipette with the solution. For rinsing, suck about 5 mL of the solution into it. Hold the pipette between two hands. Tilt and rotate it so that the inner walls of the pipette come in the contact of the solution. Allow the rinsed solution to run out into the sink. No observe the following while measuring the solution with the pipette.

(*i*) Now place the narrow tip of the pipette well below the surface of the liquid and suck the solution from the other end until the solution rises well above the circular edged mark. Now place your forefinger of the right hand at the mouth end firmly [Fig. 7.5 (*a*) and (*b*)].

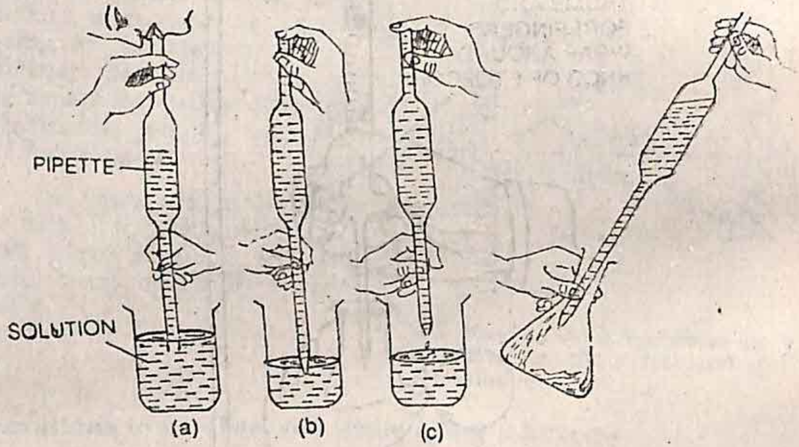


Fig. 7.5. Measuring of solution with a pipette, (*a*) Filling the pipette with a solution, (*b*) Closing of the upper end of the pipette with a forefinger, (*c*) Releasing of the solution until the level of the solution coincides with the circular mark, and (*d*) Releasing of the solution into the titration flask.

(*ii*) Now keep the tip above the level of the solution. Release the pressure gently so that liquid gradually moves downward. Continue to allow the level of the solution to fall slowly until the lower meniscus touches the etched mark when viewed by placing the eye at its level [Fig. 7·5 (*c*)].

(*iii*) Cerefully move the pipette to the titration flask and introduce its tip into the titration flask [Fig. 7.5 (*d*)]. Now release the pressure completely by removing the forefinger. Wait for a few seconds for the solution to run out completely. Do not blow it out.

(*iv*) Touch the tip of the pipette against the walls of the flask [Fig. 7.5 (*d*)] and hold it in the flask for 10 seconds. Remove the pipette.

(*v*) Students will find a drop or two still left in the jet end of the pipette. This should not be blown out because it has already been accounted for while calibrating the pipette.

Precautions to be observed while using a pipette

(*i*) Clean the pipette with chromic acid and finally wash it with distilled water.

(*ii*) Rinse the pipette properly with the solution to be delivered.

(*iii*) Never suck too fast lest the solution should rush into your mouth. Do not suck poisonous solutions into the pipette.

(*iv*) Forefinger used to hold the solution must be dry.

(*v*) Do not blow out the last drop from the tip of the pipette.

(*vi*) During sucking, the lower end of the pipette should be well below the surface of the solution, or else the solution may get into mouth.

(*vii*) A pipette with a broken tip should not be used.

(*viii*) Hot liquids should not be measured.

(*ix*) Solution level should be observed at eye-level.

(*iv*) **Graduated flasks.** They are used for preparing standard solutions. The most common sizes of the graduated flasks used in the laboratory are of 100 mL, 250 mL, 500 mL and 1000 mL capacity. Observe the following when preparing the standard solutions :

Transfer the solution or solid through a clean funnel to a clean graduated flask. Allow the washings to go into the flask and remove the funnel. Stopper the flask and shake contents well. Now add sufficient distilled water to near the graduation mark, Add the final drops of water with a pipette until the lower meniscus of the solution touches the graduation mark. Observe this at eye-level to avoid errors due to parallax. Stopper the flask and invert it several times so as to produce a homogeneous solution.

Precautions to be observed while using a graduated flask

(*i*) Always use funnel to transfer solution to the graduated flask and do not allow the funnel to rest on the neck of the latter.

(*ii*) Wash the funnel with distilled water before removing it from the graduated flask.

(*iii*) Graduated flask should never be heated. Never place hot solution into it.

(*iv*) Its stopper should not be changed.

(*v*) It should not be rinsed with solution to be stored in it.

7.4. ACID-ALKALI TITRATION (ACIDIMETRY OR ALKALIMETRY)

By acidimetry, we mean the determination of unknown strength of an alkali by titration with a standard solution. Alkalimetry is just the opposite of this statement. When an acid is mixed with an alkali, H^+ ions of the acid react with OH^- ions of the alkali to produce water. The solution can therefore be either acidic (when an excess of H^+ ions are present) or alkaline (when an excess of OH^- ions are present) or neutral (pH of the solution 7 ; neither the H^+ ions nor the OH^- ions are present in excess desired by the equivalence point). For example, in the reaction of HCl (a strong acid) with NaOH (a strong base), the condition of neutrality is reached.

$$Na^+(aq)+OH^-(aq)+H^+(aq)+Cl^-(aq) \rightarrow Na^+(aq)+Cl^-(aq)+H_2O(l)$$

The net change is

$$H^+(aq)+OH^-(aq) \longrightarrow H_2O(l)$$

When a certain amount of an acid is so treated with an alkali that it is completely converted into a normal salt and loses its acidic properties, it is said to be neutralized. The case is otherwise when the acid or the base or both are weak. The solution at the equivalence point will be either acidic or alkaline. This is due to the hydrolysis of the salt produced in the neuralization reaction.

Some salts are able to act as acids or bases. For example, ammonium salts are acidic, the ammonium ion furnishes a proton to the solvent.

$$NH_4^+(aq)+H_2O(l) \rightleftharpoons NH_3(aq)+H_3O^+(aq)$$

Carbonates abstract protons from the solvent and so act as bases.

$$CO_3^{2-}(aq)+H_2O(l) \rightleftharpoons HCO_3^-(aq)+OH^-(aq)$$

Thus the progress of any acid-base titrations would be to monitor the change in pH with an electrical pH meter. But it is customary to detect the end point of a titration with the aid of chemical indicator, a substance which changes colour when the pH of its solution alters.

Acid-alkali titrations have already been discussed at Class XI level.

7.5. REDOX TITRATIONS

Redox, *i.e.*, reduction-oxidation titrations can be conducted using reagents which behave as reducing and oxidixing reagents. These reagents are usually coloured in the oxidized or reduced forms but of a significantly different colour (or even colourless) in the other state. For example, potassium permanganate is purple in its oxidized from, but its reduced product, *i.e* , manganese (II) ion is almost colourless.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

In some cases, the colour change is not distinct to ensure accuracy. For example the iodine is brown in solution, the iodide ion is colourless.

$$I_2 + 2e^- \dashrightarrow 2I^-$$

As the iodine is reduced, the colour fades to a pale yellow which is difficult to distinguish from the colourless iodide ion. If starch is added, on intence blue colour appears in the presence of even a trace of iodine. It is colourless in the absence of iodine.

Redox titrations involve reactions in which a change in oxidation number takes place and one uses to estimate the amount of an oxidizing agent or that of a reducing agent from their solutions. In these reactions oxidation and reduction take place simultaneously. If one substance is oxidized then the other is reduced. In the following reaction MnO_4^- ions act as oxidizing agent and Fe^{2+}($FeSO_4 \cdot 7H_2O$) ions act as reducing agent. Here MnO_4^- ions, get reduced to Mn^{2+} ions and Fe^{2+} ions get oxidized to Fe^{3+} ions.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \text{ (Reduction)}$$

(From oxidizing reagent)

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \mid \times 5 \text{(Oxidation)}$$

(From reducing reagent)

$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 5H_2O$$

(Redox reaction)

7.5 POTASSIUM PERMANGANATE TITRATIONS

Potassium permanganate is usually employed in the volumetric estimation of many reducing agents such as oxalic acid, oxalates, ferrous sulphate, Mohr's salt, *etc*. The titratton is successfully carried out in the acidic medium. Among the three mineral acids available, only sulphuric acid is used because it does not act on the permanganate ion in dilute solutions.

Hydrochloric acid is not used as it reacts with $KMnO_4$.

$$2MnO_4^- + 10Cl^- + 16H^+ \longrightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$$

HCl consumes the permanganate ion in excess of that used in the oxidation of the substance that is being titrated.

Nitric acid is also not used because of its strong oxidizing nature.

Potassium permanganate solution is dark purple in colour. The colour disappears in the presence of a reducing agent. At the end of a reaction, any excess of $KMnO_4$ solution added, makes the solution pink. Thus, in this titration no indicator is required. Potassium permanganate acts as '**self indicator**'.

At times, as the end point is approached, the pink colour starts fading due to the interaction between the MnO_4^- ions and Mn^{2+} ions formed during the course of titration.

$$2MnO_4^- + 3Mn^{2+} \longrightarrow 5MnO_2 + 4H^+$$

To avoid such a reaction a sufficiently acidic medium should be used.

The reduction of permanganate may proceed to different oxidation states of manganese, depending on the solution conditions. Accordingly number of electrons involved in the reaction varies, and hence, the gram-equivalent mass of permanganate will be different for different reactions. For example, in strong acidic solution, heptavalent 'manganese' in permanganate is reduced to divalent manganese.

$$MnO^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + H_2O$$

Thus on the basis of this reaction the equivalent mass of $KMnO_4$ is 158·04/5=31·6.

In weekly acidic, alkaline or neutral solutions, heptavalent manganese is reduced to quadrivalent manganese with the formation of manganese dioxide.

$$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$$

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

In this case, the equivalent mass of $KMnO_4$ has different value; *i.e.*,

$$\text{Equivalent mass of } KMnO_4 = \frac{158.04}{3} = 52.68$$

Thus, it is clear that the equivalent mass of the substance is not fixed, but is dependent upon the reaction accompanying the titration. The equivalent mass of a few oxidizing and reducing agents commonly used in the laboratory are given in Table 7.1.

7.5.1. Calculations

Titration calculations can be reduced to a few simple steps. It is essential to know which substance is acting as the standard. The steps required are : (1) the determination of equivalent mass of the standard used on the basis of balanced chemical equation ; (2) the calculation of the normality of the standard solution ; (3) the calculation of the normality of the other solution ; and (4) the determination of the quantity (concentration, purity, *etc.*) required.

Table 7.1. Equivalent masses of commonly used substances in redox titrations.

Name of the substance	*Molecular formula*	*Molecular mass*	*Ion-electron equation*	*Number of electrons gained or lost per molecule (n)*	*Equivalent mass (M/n)*
Potassium permanganate	$KMnO_4$	158	$MnO_4^- + 8H^+ + 5e^-$ $\rightarrow Mn^{2+} + 4H_2O$	5	$\frac{158 \cdot 4}{5} = 31.6$
Ferrous sulphate	$FeSO_4.7H_2O$	278	$Fe^+ \rightarrow Fe^{3+} + 1e^-$	1	$\frac{278}{1} = 278$
Mohr's salt	$FeSO_4.(NH_4)_2SO_4.6H_2O$	392	$Fe^{2+} \rightarrow Fe^{3+} + 1e^-$	1	$\frac{392}{1} = 392$
Oxalic acid	$\begin{array}{l} COOH \\ \vert \quad 2H_2O \\ COOH \end{array}$	126	$\begin{array}{l} COO^- \\ \vert \quad \rightarrow 2CO_2 + 2e^- \\ COO^- \end{array}$	2	$\frac{126}{2} = 63$
Potassium dichromate	$K_2Cr_2O_7$	294	$Cr_2O_7^{2-} + 14H^+ + 6e^-$ $\rightarrow 2Cr^{3+} + 7H_2O$	6	$\frac{294}{6} = 49$

Calculation using normality .

The normal concentration of a solution, designated by the letter '*N*' is one of the ways of expressing the concentration of solutions. This method is based on the equivalent mass of the solute. A solution is said to be normal one, when it contains one gram equivalent of the solute per litre of the solution. The equivalent mass expressed in grams is called gram-equivalent. It is important to emphasize here that the gram-equivalent is not invariant as the gram-molecular mass is but depends upon the reaction concerned.

$$\text{Normality}=\frac{\text{Concentration in gram per litre}}{\text{Equivalent mass}}$$

Dilution problems involving normal concentrations are the same as with moral concentrations.

∴ Number of equivalents before dilution

=Number of equivalents after dilution

or
$$N_1V_1=N_2V_2$$
$$\frac{eq}{L}\times L=\frac{eq}{L}\times L$$

As we known that the number of equivalents$=NV$, so it is simply a matter of substituting 'equals for equals'. Accordingly one mL of 1 N solution of any substance will react exactly with 1 mL of 1 N solution of another substance and that solutions of equal normality will react volume for volume.

Accordingly if the solution of a substance A is titrated against the solution of a substance B then at the end point we can write as follows :

Number of gram equivalents of solution A

=Number of gram equivalents of solution B

or
$$N_1V_1=N_2V_2 \qquad \ldots(7.1)$$

where N_1 and N_2 are the normalities and V_1 and V_2 the volumes of solutions A and B respectively.

From Eq. (7.1), the normality of a unknown solution can be calculated. Let this be x. Now $N_1V_1=N_2V_2$. If N_1, V_1 and V_2 are known, $N_2=x$ can be calculated by the equation

$$x=N_2=\frac{N_1V_1}{V_2} \qquad \ldots(7.2)$$

With the known/calculated normality of a solution, its strength in grams per litre can be known by applying the following relation :

$$\text{Strength}=\text{Normality}\times\text{Equivalent mass} \qquad \ldots(7.3)$$

Calculation using molarity

The steps required are :

(1) The determination of the number of moles of the standard used ; (2) the writing of a balanced chemical equation ; (3) the calculation of the number of moles of the other compound ; (4) the conversion of the number of moles of the other compound to a mass ; and so (5) the determination of the quantity (concentration, purity, *etc.*) required.

It may be recalled that the molar solution of a substance is that solution which contains one gram molecular mass (or one mole) of it per litre of the solution.

For example, the molecular mass of HCl is 36.5. Thus, a solution containing 36.5 g of hydrochloric acid in one litre of solution will be 1.0 M. Similarly when 3·65 or 0.73 g of it are present in one litre, the molarity of the solutions will be 0.1 M or M/10 and 0.02 M or M/50 respectively. Mathematically molarity may be expressed as given below :

$$M=\frac{\text{Number of moles of solute}}{\text{Volume in litre}}$$

$$=\frac{\text{Mass of solute in g L}^{-1}}{\text{Molecular mass of solute}}$$

$$=\frac{\text{Mass of the solute in grams}}{\text{Molecular mass of solute}\times\text{Volume of solution in litre}}$$

Thus, using above relationship, the molarity of a solution can be determined if the molecular mass of the solute and the amount dissolved per litre of the solution is known. Also, the amount of solute which is to be dissolved (for preparing a solution of known molarity) can be computed from the above relationship.

$$\text{Mass of solute (in grams)}=\text{Molecular mass of the solute}\times\text{Volume of solution in litre}\times\text{molarity}$$

Relationship between normality and molarity. The concentration terms, molarity and normality can be inter-related to each other by a simple relationship given below :

$$\text{Normality}=\text{Molarity}\times\text{number of equivalents per molecular mass of the solute}$$

$$=\text{Molarity}\times\frac{\text{Molecular mass}}{\text{Equivalent mass}}$$

$$=\text{Molarity}\times\text{Number of electrons gained or lost per molecule (or ion) of the solute in a balanced equation}$$

$$N=M\times n$$

where n=Number of electrons gained or lost per molecule (or ion) in a balanced equation.

Netes on the use of potassium permanganate

Potassium permanganate is not used as a primary standard because of the following reasons :

(*i*) It is not usually obtained in a very pure state. It is found mixed with manganese dioxide.

(*ii*) The presence of manganese dioxide catalyses the auto-decomposition of $KMnO_4$ solution.

(*iii*) Moreover, $KMnO_4$ being a strong oxidizing agent a portion of the reagent is used up in oxidizing the oxidizable impurities present in reagents or distilled water. It can also undergo photochemical decomposition.

Because of the above reasons, the solution of $KMnO_4$ is filtered. Filtration is done by : (*a*) passing through a Gooch containing a pad of purified asbestos, (*b*) passing through a plug of purified glass wool in a funnel ; *etc*.

$KMnO_4$ solution is usually stored in coloured bottles to prevent the effect of light.

From this it follows that standard permanganate solution cannot be prepared by exact weighing and cannot be stored for a long time. In practice, therefore, a solution of the approximate strength (required) is prepared and then standardized against the solution of a primary standard.

The solution of potassium permanganate is generally taken in a burette when standardizing it. It is advised to use the burette with a glass stop cock instead of a rubber pinch cock as rubber is slowly attacked by potassium permanganate on standing. As $KMnO_4$ is deeply coloured, always read the upper meniscus while taking the burette reading, Addition of $KMnO_4$ solution with stirring is also advised to avoid the precipitation of hydrated manganese dioxide, which intereferes in arriving at the correct end point.

7.6. EXPERIMENTS

Experiment 7.1. To determine the strength of $KMnO_4$ solution using standard oxalic acid solution.

Apparatus : Burette, conical flask, pipette, graduated flask, *etc*.

Chemicals : Oxalic acid, $KMnO_4$ solution, H_2SO_4 (dilute), distilled water.

General : In this method a hot solution of oxalic acid acidified with dilute sulphuric acid is titrated slowly with potassium permanganate solution until a light pink colour appears in the solution. The reaction is as follows :

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Procedure. It involves the following steps :

(*i*) **Preparation of standard oxalic acid.** Weigh out accurately oxalic acid crystals in a weighing bottle or a watch glass. (0.787 g for 250 mL 0.05 N solution). Transfer to a 250 mL measuring flask. Dissolve the crystals of oxalic acid in distilled water by shaking and then make up the solution up to the mark with more of distilled water. Again, shake the flask gently up and down to ensure through mixing.

(*ii*) **Titration of $KMnO_4$ solution with oxalic acid.** Rinse the burette with potassium permanganate solution and fill it up to a convenient mark. Pipette out 20 mL of the standard solution of oxalic (N/20) into a titration flask and add to it ~ 10 mL of dilute sulphuric acid. Heat the flask on a wire gauze to 60–70°C. Note the initial reading of the burette by noting the upper meniscus. Now run the potassium permanganate solution slowly in small amounts at a time to the hot solution with stirring until the end point (pink colour) is reached. Note the final reading of the burette by noting the upper meniscus only.

Repeat the above titration until three concordant readings are obtained.

Indicator—Not required.

Normality of the oxalic acid solution = 0.05 N

Observations

S.No.	*Volume of oxalic acid solution taken* (mL)	*Burette reading*		*Volume of $KMnO_4$ solution* (mL)
		Initial	*Final*	
1.	20.0			
2.	20.0			
3.	20.0			
4.	20.0			

Calculations

Suppose 20 mL of 0.05 N oxalic acid

$$\equiv V \text{ mL of } KMnO_4 \text{ solution}$$

or $$20 \times 0.05 \text{ N} = V \times N_{KMnO_4}$$

or $$N_{KMnO_4} = \frac{1.0}{V}$$

and $$\text{Strength} = \text{Normality} \times \text{eq. mass of } KMnO_4$$

$$= \frac{1.0}{V} \times 31.6 \text{ g/L}$$

Experiment 7.2. To determine the strength of the given sample of $KMnO_4$ solution in g/L. Prepare a standard solution of 0.05 N Mohr's salt [$FeSO_4(NH_4)_2SO_4 6H_2O$].

Apparatus : As given in Experiment 7·1.

Chemicals : Mohr's salt, $KMnO_4$, distilled water, H_2SO_4.

General. In this method, a solution of Mohr's salt acidified with dilute sulphuric acid is titrated with potassium permanganate solution at normal temperature until a permanent pink coloured solution appears. The reaction is as follows :

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Procedure. It involves the following steps :

(*i*) **Preparation of standard Mohr's salt solution**. Weigh out accurately pure Mohr's salt crystals in a weighing bottle (1.96 g for 100 mL 0.05 N solution). Transfer it to a 100 mL measuring flask which is already having a few drops of concentrated sulphuric acid. Then add 50 mL of distilled water. Dissolve it by shaking and then make up the volume upto the mark on the flask by adding distilled water.

(*ii*) **Titratian of $KMnO_4$ solution with Mohr's salt solution**. Rinse and fill the burette with the given solution of potassium permanganate and read the initial reading of the burette by noting the upper meniscus only.

Pipette out 10 mL of Mohr's salt solution in a conical flask. To this add 10 mL of dilute sulphuric acid. Run $KMnO_4$ solution from the burette into the conical flask until a permanent light pink colour is developed in solution. Repeat such titrations until three concordant readings are obtained. Record the observations as suggested in Experiment 7·1.

Calculations

Suppose 10 mL 0.05 N Mohr's salt solution$\equiv V$ mL of $KMnO_4$ solution

Therefore $10 \times 0.05 = V \times N_{KMnO_4}$

$$N_{KMnO_4} = \frac{0.5}{V}$$

Strength of $KMnO_4 = \frac{0.5}{V} \times 31.6$ g/L

Note. It is not necessary to weigh exactly the same amount as required for the preparation of exact 0.05 N oxalic acid or Mohr's salt. The usual practice is to weigh accurately a small amount of solid substance in a analytical balance and then dissolve it in distilled water in a 100 mL (or 250 mL) measuring flask. Now calculate the exact normality of the solution by applying the following formula if the total solution prepared is 100 mL.

Normality of the given solution

$$= \frac{10 \times \text{Amount of the substance dissolved}}{\text{Equivalent mass of the substance}}$$

Experiment 7.3. To determine the number of water molecules of crystallization in oxalic acid crystals ($H_2C_2O_4.xH_3O$), M g of which is present in one litre of solution. Provided 0.05 N $KMnO_4$ solution.

Procedure. Rinse and fill the burette with 0.05 N $KMnO_4$ solution. Pipette out 10 mL of oxalic acid solution in a conical flask. To this add 10 mL of dilute sulphuric acid. Heat the solution to 60-70°C and titrate against $KMnO_4$ solution until a light pink colour is obtained. Repeat the titration till concordant values are obtained.

Calculation. Let M g of hydrated oxalic acid has been dissolved to make one litre solution.

Therefore, the strength of hydrated salt$=M$ g/L

Let V mL of 0·05 N $KMnO_4 \equiv 10$ mL of oxalic acid solution

$$V \times \frac{N}{20} = 10 \times N_{\text{oxalic acid}}$$

or

$$N_{\text{oxalic acid}} = \frac{V}{200}$$

$$\text{Strength of anhydrous salt} = \frac{V}{200} \times 45 \text{ g/L}$$

We know,

$$\frac{\text{Strength of hydrated salt}}{\text{Strength of anhydrous salt}} = \frac{\text{Mol. mass of hydrated salt}}{\text{Mol. mass of anhydrous salt}}$$

$$\frac{M}{\frac{V}{200} \times 45} = \frac{90 + 18x}{90}$$

From this equation, calculate the value of x.

Experiment 7.4. To determine the number of water molecules of crystallization in ferrous sulphate crystals ($FeSO_4.xH_2O$), M g of which is present in one litre of solution. You are provided with a solution of 0.05 N $KMnO_4$ solution.

Procedure. Rinse and fill the burette with 0.05 N $KMnO_4$ solution. Pipette out 10 mL of the ferrous sulphate solution in a conical flask. To this add 10 mL of dilute sulphuric acid. Now titrate it with $KMnO_4$ solution until a light pink colour appears. Repeat the titration till concordant are obtained.

Calculations. Suppose M g of hydrated ferrous sulphate has been dissolved to make 1 litre solution.

Therefore, the strength of hydrated salt $= M$ g/L

Let V mL of 0·05 N $KMnO_4 \equiv 10$ mL of ferrous sulphate solution

$$V \times \frac{N}{20} = 10 \times N_{FeSO_4}$$

or

$$N_{FeSO_4} = \frac{V}{200}$$

Strength of anhydrous $FeSO_4$ salt $= \frac{V}{200} \times 152$

We know

$$\frac{\text{Strength of hydrated salt}}{\text{Strength of anhydrous salt}} = \frac{\text{Mol. mass of hydrated salt}}{\text{Mol. mass of anhydrous salt}}$$

$$\frac{M}{\frac{V}{200} \times 152} = \frac{152 + 18\,x}{152}$$

From the above expression one gets the value of x.

ORAL QUESTIONS AND ANSWERS

Q. 7.1. What do you mean by volumetric analysis ?

Ans. The analysis which involves exact measurement of volume of titre and titrant is termed as volumetric analysis.

Q. 7.2. What do you mean by titration ?

Ans. It is a process of running out a solution from a burette into a solution contained in a conical flask or a beaker until the reaction is complete. The completion of the reaction is monitored by the use of indicator or some other method.

Q. 7.3. What is an indicator ?

Ans. A substance used to determine the end point of a reaction is termed as indicator. It changes colour over a range of pH.

Q. 7.4. What is a standard solution ?

Ans. A solution of exactly known strength is called a standard solution.

Q. 7.5. What is a normal solution ?

Ans. A solution which contains one gram equivalent mass of a solute dissolved per litre of the solution is termed as normal solution.

Q. 7.6. What is normality equation ?

Ans. According to the law of equivalents the number of equivalents of a substance (say acid) reacts with the equal number of equivalents of another substance (say base).

Therefore, $N_1V_1=N_2V_2$

This is called the normality equation.

Q. 7.7. What is an titrant ?

Ans. The solution which is filled in the burette is called titrant. Usually its strength is known.

Q. 7.8. What is a titre ?

Ans. The solution which is kept in the conical flask for titration purposes. Its strength is normally to be determined.

Q. 7.9. What is an end point ?

Ans. The stage at which the colour change of the indicator is visible to the eye is callled the end point.

Q. 7.10. What is a molar solution ?

Ans. A solution containing one mole of the solute per 1000 mL of the solution is called a molar solution.

Q. 7.11. What is a primary standard ?

Ans. A chemical substance which can be used directly for preparing the standard solution. It does not experience any chemical change at room temperature.

Q. 7.12. What is a decinormal solution ?

Ans. A 0·1 N solution is called a decinormal solution.

Q. 7.13. What is the strength of a solution ?

Ans. It is the quantity of a solute present in one litre of the solution. It is found out by the expression,

$$\text{Strength}=\text{Normality}\times\text{Equivalent mass}$$

It is expressed in g/L.

Q. 7.14. What is redox titrations ?

Ans. The titration which involves a redox reaction, *i.e.* simultaneous oxidation and reduction, is called a redox titration.

Q. 7.15. Is $KMnO_4$ a primary standard ? Comment.

Ans. No. It gets decomposed to MnO_2 with time. It may also react with organic matter present in water used for preparing the solution.

Q. 7.16. How will you prepare a standard solution of potassium permanganate ?

Ans First of all, a solution of approximate strength is prepared which in turn is standardized against a standard solution of oxalic acid or Mohr's salt. Then, it is diluted to a known volume to get a standard solution of known strength

It is important to note that the solution of $KMnO_4$ is always made fresh as the organic water present in water reduce it to MnO_2. Further $KMnO_4$ solution should not be filtered through filter paper as its organic matter will reduce $KMnO_4$. $KMnO_4$ solution should be filtered through glass wool, *etc.*

Q. 7.17. Permanganate reaction depends upon the conditions of the solution. Comment.

Ans. In acidic medium, the reaction of $KMnO_4$ is

$$MnO_5^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

In basic medium, the reaction is

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

Since the number of electrons involved in the two reactions is different, the gram-equivalent mass of permanganate, will be different in acidic and alkaline conditions.

Q. 7.18. How is the burette reading taken when it is filled with potassium permanganate solution ?

Ans. It is advisable to read the upper meniscus when the dark coloured solution like $KMnO_4$ solution is filled in a burette.

Q. 7.19. Why is $KMnO_4$ solution not taken in a burette with a rubber tube ?

Ans. Rubber, being organic in nature reduces $KMnO_4$ to MnO_2.

Q. 7.20. Why is dil. H_2SO_4 the most suitable acid as compared to HCl and HNO_3 in $KMnO_4$ titrations ?

Ans. Because H_2SO_4 does not act on the MnO_4^{1-} ion in dilute solutions. HCl acts as a reducing agent while HNO_3 is an oxidizing agent.

Q 7 21. What is the oxidation number of manganese in $KMnO_4$?

Ans. Oxidation number of manganese in $KMnO_4$ is +7.

Q. 7.22. In a glass container in which a permanganate solution is kept for a long time, a brown deposit is seen on the wall. Comment.

Ans. $KMnO_4$ is reduced to MnO_2 which gets deposited on the walls.

Q. 7.23. Oxalic acid solution is heated to 70°C when titrated against $KMnO_4$ solution. Comment.

Ans. Heating is done to enhance the rate of the reaction and speed up the rate of formation of Mn^{2+} ions, which act as catalyst.

Higher temperature may decompose the oxalic acid into carbon dioxide and corbon monoxide.

Q. 7.24. The ferrous ion-permanganate titration is done in cold. Comment.

Ans. Ferrous ion is oxidized to ferric ion by oxygen of air at higher temperatures. The titration involving Fe^{2+} ions is done in cold solution only.

Q. 7.25. Why is dilute sulphuric acid added while preparing standard solution of Mohr's salt ?

Ans. It is added to prevent hydrolysis of ferrous ions.

Q. 7.26. Why is brown turbidity sometimes observed in the titration flask while titrating $KMnO_4$ solution with oxalic acid ?

Ans. Brown colour or a precipitate may be formed due to the following reasons :

(*i*) Solution is cold.

(*ii*) Potassium permanganate solution has been added too quickly.

(*iii*) Sulphuric acid is not present in sufficient quantity.

Q. 7.27. Why is Mohr's salt used in place of hydrated ferrous sulphate for preparing standard solution ?

Ans. There are two reasons for this :

(*i*) Ferrous sulphate being efflorescent in nature, loses its water of crystallization on exposure to air. Its composition therefore does not correspond to molecular formula. On the other hand, Mohr's salt is not efflorescent. Therefore, its composition is fixed.

(*ii*) Ferrous sulphate is easily oxidized to basic ferric sulphate when exposed to air. On the other hand, ferrous ammonium sulphate is stable and does not oxidize.

Because of the reasons given, Mohr's salt is used for preparing standard solutton.

Q. 7.28. How will you wash the glass apparatus which has become coloured on storing potassium permanganate solution in it ?

Ans. It is advised to wash the container first with water, then with dilute ferrous sulphate solution and finally with water.

□ □

UNIT 8

Qualitative Analysis—Identification of Cations and Anions Present in a Mixture

8.1. INTRODUCTION

A substance is analysed to establish its qualitative or quantitative chemical composition. An anyalsis that yields information only as to the identity of the ingredients is known as qualitative analysis. Qualitative analysis of inorganic substances is primarily concerned with the detection and identification of the ions present in a substance (a single substance/salt or a mixture of substances/salts). The salts, on dissolution in water, spilt into positively charged ions called cations and negatively charged ions called anions. The cation is also known as basic radical and the anion as acid radical.

In qualitative analysis, in order to identify the ions of a substance being analysed, other substances (solids, solutions, *etc.*) called reagents are added to it that cause chemical transformations accompanied with the formation of new compounds possessing specific properties : a definite physical state (precipitate, liquid, gas) ; certain solubility in water, acids, alkalis and other chemical solvents, a characteristic colour, odour and so forth.

The following principles has a great bearing upon the operations usually followed in qualitative analysis, law of mass action, common ion effect, solubility product, complex ion formation, pH, *etc.*

A reaction used in qualitative analysis must :

1. occur rapidly, practically instantanously,
2. be accompanied with the formation of a characteristic precipitate, gas or with the appearance of a colour,
3. be practically irrevesible, *i.e.*, occur mainly in one direction, and
4. be specific, if possible, and highly sensitive.

In our scheme of qualitative analysis, we shall analyse the salts for the following cations and anions :

Cations. Lead (II) Pb^{2+}, mercury (II) Hg^{2+}, copper (II) Cu^{2+}, cadmium (II) Cd^{2+}, arsenic (III) As^{3+}, antimony (III) Sb^{3+}, iron (II) Fe^{2+}, iron (III) Fe^{3+}, aluminium (III) Al^{3+}, nickel (II) Ni^{2+}, cobalt (II) Co^{2+}, manganese (II) Mn^{2+}, zinc (II) Zn^{2+}, calcium (II) Ca^{2+}, barium (II) Ba^{2+}, strontium (II) Sr^{2+}, magnesium (II) Mg^{2+}, potassium (I) K^+, and ammonium (I) NH_4^+.

Anions. Carbonate, CO_3^{2-} ; sulphite, SO_3^{2-} ; sulphide, S^{2-} chloride, Cl^- ; bromide, Br^- ; iodide, I^- ; nitrite, NO_2^- ; nitrate, NO_3^-; sulphate, SO_4^{2-} ; phosphate, PO_4^{3-} ; and acetate, CH_3COO^-.

For identification purposes, two cations of the same group and anion combinations such as $(SO_4^{2+}+SO_3^{2-})$, $(NO_2^-+NO_3^-)$, (Cl^-+Br^-), *etc.* are not included.

8.2. SYSTEMATIC ANALYSIS

The salt analysis may be systematically carried out in the following steps :

(*i*) Preliminary examination,
(*ii*) Detection of anions, and
(*iii*) Detection of cations.

8.3. PRELIMINARY EXAMINATION

In qualitative analysis, various characteristic features of the chemical substances being analysed are used for establishing its chemical composition. For example, ammonia can easily be identified by its characteristics smell and ammonium salts by the liberation of ammonia gas when the salts are heated with caustic soda.

In some cases, substances are tested by dry analysis, *i.e.*, without transferring them into solution. Such an analysis usually consists the examination of physical properties of the salt/mixture. It involves the heating of a substance to give a gas with a distinct smell and colour. It also consists in testing the ability of a salt/mixture to give a characteristic colour to a colourless flame or a certain colour to a melt (bead or glass) obtained when heating the substance with borax in the eye of platinum wire.

8.3.1. Physical Properties

The physical properties of a salt mixture, *viz.*, colour, appearance and odour, *etc.* help in arriving at an inference regarding the salt mixture as given in Table 8·1.

8.3.2. Action of Heat

A substance on heating may sublime, decompose with evolution of gas, or undergo certain other changes. Careful observation of the changes and recognition of the gases evolved help us in arriving at some result (Table 8.2).

Further the colour of a salt/mixture indicates its constituents, *e.g.*, copper carbonate is green, copper sulphide is black, cadmium sulphide is yellow, ferric hydroxide is brown and manganese sulphate is pink.

Table 8.1. Physical properties of salts/mixtures

Physical property	*Inference*
White colour (colourless)	Pb^{2+}, Al^{3+}, Zn^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+} or NH_4^+ salt may be present
Bluish or bluish green colour	Cu^{2+} or Ni^{2+} salt
Light green colour	Fe^{2+} or Ni^{2+} salt
Yellowish brown colour	Fe^{3+} salt
Light pink/buff colour	Mn^{2+} salt
Pink or dark pink	Co^{2+} salt
Smell of ammonia gas	NH_4^+ salt
Smell of hydrogen sulphide gas	S^{2-} salt
Smell of sulphur dioxide gas	SO_3^{2-} salt
Deliquescent nature	Cl^- or NO_3^- salt may be present.

Table 8.2. Action of heat on salts/mixtures

Observation	*Inference*	*Chemistry involved*
Salt appears to be melting	Presence of some hydrated salt	Hydrated salt dissolves in its water of crystallization and appears to have melted.
White sublimate	NH_4^+ salt may be present	Some ammonium salt decomposes on heating leaving behind a sublimate : $(NH_4)_2SO_4(s) \longrightarrow NH_3(g) + NH_4HSO_4(s)$
Ammonia evolves, detected by smell	NH_4^+ salt	Ammonium salts decomposes on heating to give ammonia : $(NH_4)_2CO_3(s) \longrightarrow NH_3(g) + CO_2(s) + H_2O(g)$
Carbon dioxide gas evolves, detected by allowing the gas to pass through lime water	Lime water turns milky, CO_3^{2-} present	Carbonates decompose on heating to give carbon dioxide : $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$ $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$
Sulphur dioxide gas evolves, detected by a filter paper soaked in	Paper turns green, SO_3^{2-}, $S_2O_3^{2-}$, or SO_4^{2-} may be present	Some sulphites, thiosulphates and sulphates decompose to give sulphur dioxide :

Observation	*Inference*	*Chemistry involved*
$K_2Cr_2O_7$ solution		$2FeSO_4(s) \longrightarrow Fe_2O_3(s) + SO_2(g) + SO_3(g)$ $2CuSO_4(s) \longrightarrow 2CuO(s) + 2SO_2(g) + O_2(g)$
Nitrogen dioxide gas evolves, detected by its colour and irritating smell	NO_3^- present	Nitrates decompose to give nitrogen dioxide : $2Cu(NO_3)_2(s) \longrightarrow 2CuO(s) + O_2(g) + 4NO_2(g)$
Colour of the salt changes from		
(*i*) blue to white	Cu^{2+} salt	Some salts change the colour either by losing water of crystallization or due to the change in state : $\underset{\text{(Blue)}}{CuSO_4\,5H_2O(s)} \longrightarrow \underset{\text{(White)}}{CuSO_4(s)} + 5H_2O(g)$
(*ii*) green to yellow	Ni^{2+} salt	
(*iii*) yellow (when hot) to white (when cold)	Zn^{2+} salt	

8.3.3. Flame Test

Certain cations can be identified by the colour which they impart to the colourless flame of burner ; sodium salts turn it yellow ; potassium salts, voilet ; calcium salts, brick red ; barium salts, green ; copper salts, blue-green ; and so forth. Thus, this property can be helpful in identifying the various metal ions. For a particular element the flame colouration remains the same irrespective of whether the element is in the free state or combined with other elements. For example, metallic copper, copper sulphate, copper nitrate, copper chloride and copper carbonate all impart blue-green colour to the flame. The colour is characteristic of copper in all its forms. The flame test is usually carried out with the chloride of the metal as it is more volatile than other salts. The given salt is treated with concentrated hydrochloric acid (to convert it into the chloride form) and placed in the eye of platinum or nichrome wire. The wire is then heated in an oxidizing (non-luminous) flame when it imparts a characteristic colour to the flame

Table 8.3. Flame Test

Flame colour by naked eye	*Flame colour through blue glass*	*Inference*
Deep blue green	Bluish green	Cu^{2+}
Brick red	Light yellow	Ca^{2+}
Apple green	Bluish green	Ba^{2+}
Crimson (deep red)	Purple	Sr^{2+}
Violet	Pink	K^+

(Table 8.3). Platinum or nichrome wire is suitable for the flame test because it neither melts nor imparts colour to the flame. Ordinary salts may be associated with an impurity of a sodium salt and give a yellow flame for short duration. To overcome this difficulty, the flame may also be viewed through blue glass (cobalt glass) which absorbs the yellow sodium light.

Procedure for the flame test. Make a circular loop (eye) at the end of a platinum (or nichrome) wire sealed in a glass tube. Dip it into concentrated hydrochloric acid and heat it in a non-luminous flame. Repeat this process until the platinum wire imparts no colour to the flame.

Prepare a paste of the salt with conc. hydrochloric acid in a watch glass. Take a small amount of the paste in the eye of the wire and heat in the oxidizing flame (Fig. 8.1). The salt melts in the burner flame, forming a bead. The bead is dipped for an instant into paste. Chloride compounds being volatile produce a coloured flame. First observe the colour imparted to the flame with the naked eye and then through the blue glass.

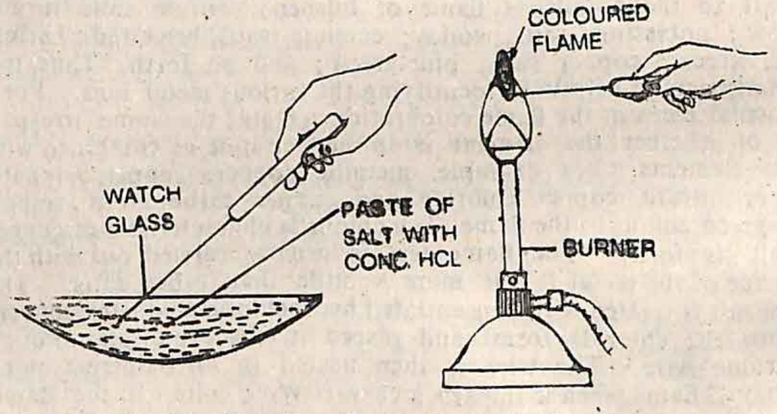


Fig. 8.1. Detection of some elements by flame test—carrying out a test.

Notes about flame test

1. The order of appearance of colour in the flame is (*i*) Na^+, (*ii*) K^+, (*iii*) Cu^{2+}, (*iv*) Ca^{2+}, (*v*) Sr^{2+} and (*vi*) Ba^{2+}.

2. Presistent golden yellow colour of sodium usually conceals all other colours of flames. When all the sodium is removed, the other flames make their appearance.

3. Everytime this test should be performed with a thoroughly cleaned wire, so that any salt adhering to it does not impart its colour to the flame.

4. Never dip the platinum wire into the bottle of conc. HCl for cleaning it. Always use a few mL of the conc. acid in a test tube for this purpose. The acid after use should be thrown into the sink.

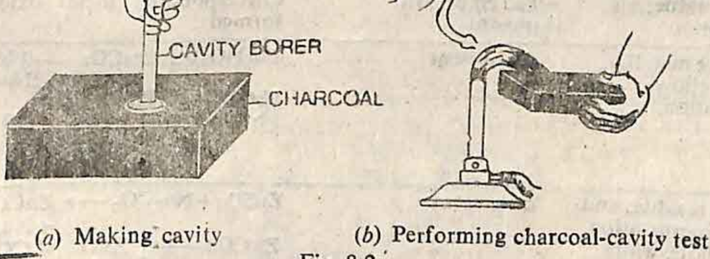
5. Do not use the acid, which is employed for cleaning platinum wire, for making paste of mixture.

8.3.4. Charcoal Cavity Test

This test is carried out for the detection of the cation present in a salt mixture. On heating the mixture of the salt and sodium carbonate (or fusion mixture) in a charcoal cavity, the metal carbonate is formed by double decomposition. The carbonate on further heating decomposes to the oxide, which is left as a coloured residue in the cavity. The colour of the residue is characteristic of the metal present. The metallic oxide, at times, is reduced to the metal by the reducing action of the charcoal resulting in the formation of metallic bead. The metal formed may also form an oxide with oxygen present in air. The oxide deposits in the form of layer or crust around the cavity called **incrustation**. The colour of the residue, bead or incrustation helps in identifying the metal.

Procedure for charcoal cavity test. Make a small cavity in a charcoal-block with a knife or cavity borer [Fig. 8.2 (*a*)]. Fill the cavity with the mixture of the salt (1 part) and sodium carbonate or fusion mixture (2 parts).

Moisten the mixture with a drop of water. Hold the charcoal block in the left hand and deflect the reducing flame* upon it with



(*a*) Making cavity (*b*) Performing charcoal-cavity test

Fig. 8.2.

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*To obtain a **reducing flame** make the bunsen-burner flame luminous by closing the air holes of the burner. Keep the nozzle of the blow pipe just outside the flame and blow gently on to the cavity.

the help of a blow-pipe for about two minutes [Fig. 8·2 (*b*)]. Observe the colour of the incrustation (a crust around the cavity) and the residue (hot and cold). At time metallic bead formation takes place. Draw the inference (Table 8·4).

Notes about charcoal cavity

1. Always make a fresh cavity for a fresh salt.

2. While making a cavity do not apply pressure otherwise it is likely to crack.

3. Do not make a very deep cavity and there should be some space around it for incrustation to form.

4. While performing charcoal cavity test always moisten the mixture with a drop of water otherwise the mixture is likely to be blown away.

Table 8.4. Charcoal cavity test

Observation	*Inference*	*Chemistry involved*
White residue, no incrustation	Al, Ca, Ba, Sr or Mg present	Corresponding metal oxide is formed *e.g.*, $2Al+3O_2 \longrightarrow Al_2O_3$
Red residue, no incrustation	Cu present	$CuSO_4+NaCO_2 \longrightarrow CuCO_3 + Na_2SO_4$ $CuCO_3 \longrightarrow CuO+CO_2$ $CuO+C \longrightarrow \underset{\text{(Red)}}{Cu} + CO$
Brown residue, brown incrustation	Cd present	$CdSO_4+Na_2CO_3 \longrightarrow CdCO_3 + Na_2SO_4$ $CdCO_3 \longrightarrow \underset{\text{(Brown)}}{CdO} + CO_2$
Black residue, no incrustation	Fe, Ni or Mn present	Corresponding metal oxide is formed
Shinning metallic bead, yellow incrustation	Pb present	$Pb(NO_3)_2+Na_2CO_3 \longrightarrow PbCO_3 + 2NaNO_3$ $PbCO_3 \longrightarrow PbO+CO_2$ $PbO+C \longrightarrow \underset{\text{(Metallic bead)}}{Pb} + CO$
Yellow residue, and yellow incrustation (when hot), white residue and white incrustation (when cold)	Zn present	$ZnSO_4+Na_2CO_3 \longrightarrow ZnCO_3 + Na_2SO_4$ $ZnCO_3 \longrightarrow \underset{\text{(Residue)}}{ZnO} + CO_2$ $ZnO+C \longrightarrow Zn+CO$ $2Zn+O_2 \longrightarrow \underset{\text{(Incrustation)}}{2ZnO}$

8.3.5. Cobalt Nitrate Test

This is an extension of the charcoal cavity test. This test is performed only when a white residue is formed in the cavity. Add a drop of cobalt nitrate solution over the white residue. Heat it again in the non-luminous (oxidizing) flame with the help of a blow pipe. Note the colour of the residue formed and draw the inference (Table 8.5).

8.3.6. Borax-bead Test

This test is used for the detection of cations in coloured salts of copper, iron, nickel and manganese.

When borax ($Na_2B_4O_7$ $10H_2O$) is heated, it fuses, loses water of crystallization and swells up into a white porous mass which then melts into a clear transparent glassy bead, composed of sodium metaborate and boric anhydride.

$$Na_2B_4O_7.10H_2O \xrightarrow{\text{Heat}} Na_2B_4O_7 \xrightarrow{\text{Red heat}} \underset{\text{(Glassy bead)}}{2NaBO_2} + B_2O_3$$

Table 8.5. Cobalt nitrate test

Observation	*Inference*	*Chemistry involved*
Blue residue	Aluminium salt	$2Co(NO_3)_2 \longrightarrow 2CoO+4NO_2+O_2$ $CoO+ \underset{\text{(Al oxide in cavity)}}{Al_2O_3} \longrightarrow \underset{\text{(Blue residue)}}{Co(AlO_2)_2}$
Pink residue	Magnesium salt	$2Co(NO_3)_2 \longrightarrow 2CoO+4NO_2+O_2$ $CoO+ \underset{\text{(Mg oxide in cavity)}}{MgO} \longrightarrow \underset{\text{(Pink residue)}}{CoO.MgO}$
Green residue	Zinc salt	$2Co(NO_3)_2 \longrightarrow 2CoO+4NO_2+O_2$ $CoO + \underset{\text{(Zn oxide (in cavity)}}{ZnO} \longrightarrow \underset{\text{(Green residue)}}{CoZnO_2}$

When this bead is heated with coloured mixture, a characteristic coloured bead of metaborate (metal oxide from metal salt reacts with bead) is formed. Thus with copper salts a green metaborate (while hot) is obtained in the oxidizing flame :

$$CuSO_4 \longrightarrow CuO+SO_3$$
$$CuO+B_2O_3 \longrightarrow \underset{\substack{\text{Cupric metaborate} \\ \text{(Blue green)}}}{Cu(BO_2)_2}$$

In reducing flame, higher metaborates are reduced to lower metaborates or metal, consequently colour changes may occur. Thus in case of cupric metaborate the following changes occur in the reducing flame.

$$2Cu(BO_2)_2 + \underset{\text{(From reducing flame)}}{C} \longrightarrow \underset{\substack{\text{Cuprous metaborate} \\ \text{(Colourless)}}}{2CuBO_2} + B_2O_3+CO$$

$$2CuBO_2+C \longrightarrow \underset{\text{(Reddish)}}{2Cu} + B_2O_3+CO$$

Procedure for a borax bead test. Take a platinum wire and make a loop at the end of the wire. Heat the loop in flame and dip it into borax powder taken in a watch glass. Heat it again, when the borax swells up and then melts to form a colourless, transparent bead which fills the loop completely. If the bead is not colourless and transparent, jerk it off, and prepare the bead again. Now bring the hot bead in the contact of a coloured salt and heat it again, first in oxidizing flame [Fig. 8.3 (*a*)] and then in a reducing flame [Fig. 8.3 (*b*)]. Note the colour of the bead in each case (hot and cold) and draw the inference (Table 8.6).

Notes about borax bead test

1. Before touching the borax bead with the test salt or mixture, make sure that the bead is transparent and colourless. If it is

Table 8.6. Borax-bead test

Observation		*Inference*	*Chemistry involved*
In oxidizing flame	*In reducing flame*		
Green when hot blue when cold	—	Copper	$CuSO_4+\underset{\text{(From bead)}}{B_2O_3} \longrightarrow \underset{\text{(Green when hot, blue when cold)}}{Cu(BO_2)_2}+SO_3$
—	Colourless when hot, red when cold	Copper	$2Cu(BO_2)_2+C \longrightarrow \underset{\text{(Colourless when cold)}}{2CuBO_2}+B_2O_3+CO$ $2CuBO_2+C \longrightarrow \underset{\text{(Red when hot)}}{2Cu}+B_2O_3+CO$
Reddish brown when hot, yellow when cold	Yellow when hot, green when cold	Iron	In both the types of flames $Fe(BO_2)_2$ is formed
Violet, hot or cold	Colourless, hot or cold	Manganese	In both the types of flames $Mn(BO_2)_2$ is formed
Brown, hot or cold	—	Nickel	$Ni(BO_2)_2$ is formed
—	Grey when cold	Nickel	Metallic nickel is obtained

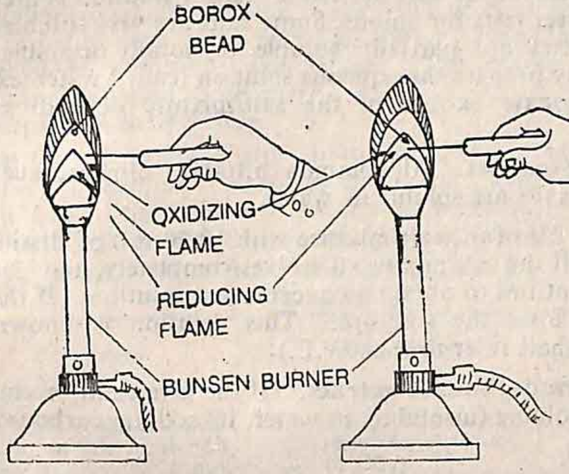


Fig. 8.3. Carrying out a borax-bead test.

coloured, the platinum wire is not clean. In such cases, jerk off the bead by a tap with your finger at the glass rod carrying wire. Prepare a fresh bead once again until it is colourless and transparent.

2. Do not perform this test with a colourless salt or mixture.

3. Always use a very small amount of the coloured salt or mixture.

4. The students should keep in mind that colour of the bead changes with temperature.

The physical examination and dry tests, thus, can help in identifying the anion and cation present in a given salt. However, it is essential that wet tests should be performed to confirm their presence. We shall now proceed with the identification of the anion present in the salt mixture.

8.4. DETECTION OF ANIONS

Anions or identifying purposes, are divided into three groups :

(*i*) **Dilute sulphuric acid group.** This group includes carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), sulphite (SO_3^{2-}), sulphide (S^{2-}) and nitrite (NO_2^-) anions.

(*ii*) **Concentrated sulphuric acid group.** This group includes chloride (Cl^-), bromide (Br^-), iodide (I^-), nitrate (NO_3^-) and acetate (CH_3COO^-) anions.

(*iii*) **A group not identified by dilute or concentrated sulphuric acid.** This includes sulphate (SO_4^{2-}) and phosphate (PO_4^{3-}) anions. They are identified by other reagents.

Preparation of salt solution. A salt solution is prepared for performing wet tests for anions. Some salts are very soluble in water, whereas others are partially soluble or totally insoluble in water. Thus, we may prepare the aqueous solution (called water extract) or sodium carbonate extract of the salt/mixture depending upon its solubility.

Water extract. All common nitrates, nitrites, acetates and many other salts are soluble in water.

Boil 1-2 g of the salt/mixture with 10-20 mL of distilled water for 5 min. If the salt/mixture dissolves completely, add more of it in small quantities to obtain a concentrated solution. If there is any suspension, filter the solution. This solution is known as water extract (we shall refer to it as W.E.).

Sodium carbonate extract. If the given salt/mixture is not completely soluble (insoluble) in water, its sodium carbonate extract is prepared.

Take 1-2 g of the salt/mixture and 4-8 g of sodium carbonate in a china dish. Add about 20 mL of distilled water and boil for about 20 min [Fig. 8.4 (*a*)]. Filter when hot [Fig. 8.4 (*b*)]. The filtrate thus obtained is called sodium carbonate extract (we shall refer to it as S.E.).

On boiling the salt/mixture with water and sodium carbonate, double decomposition takes place forming carbonate of metallic part (insoluble) and sodium salt of the acid radical (soluble). For example, when a mixture containing insoluble barium phosphate salt is boiled with sodium carbonate solution, barium carbonate (insoluble) and sodium phosphate (soluble) are formed.

$$Ba_3(PO_4)_2 + 3Na_2CO_3 \longrightarrow \underset{\textbf{(Insoluble)}}{3BaCO_3} + \underset{\textbf{(Soluble)}}{2Na_3(PO_4)_2}$$

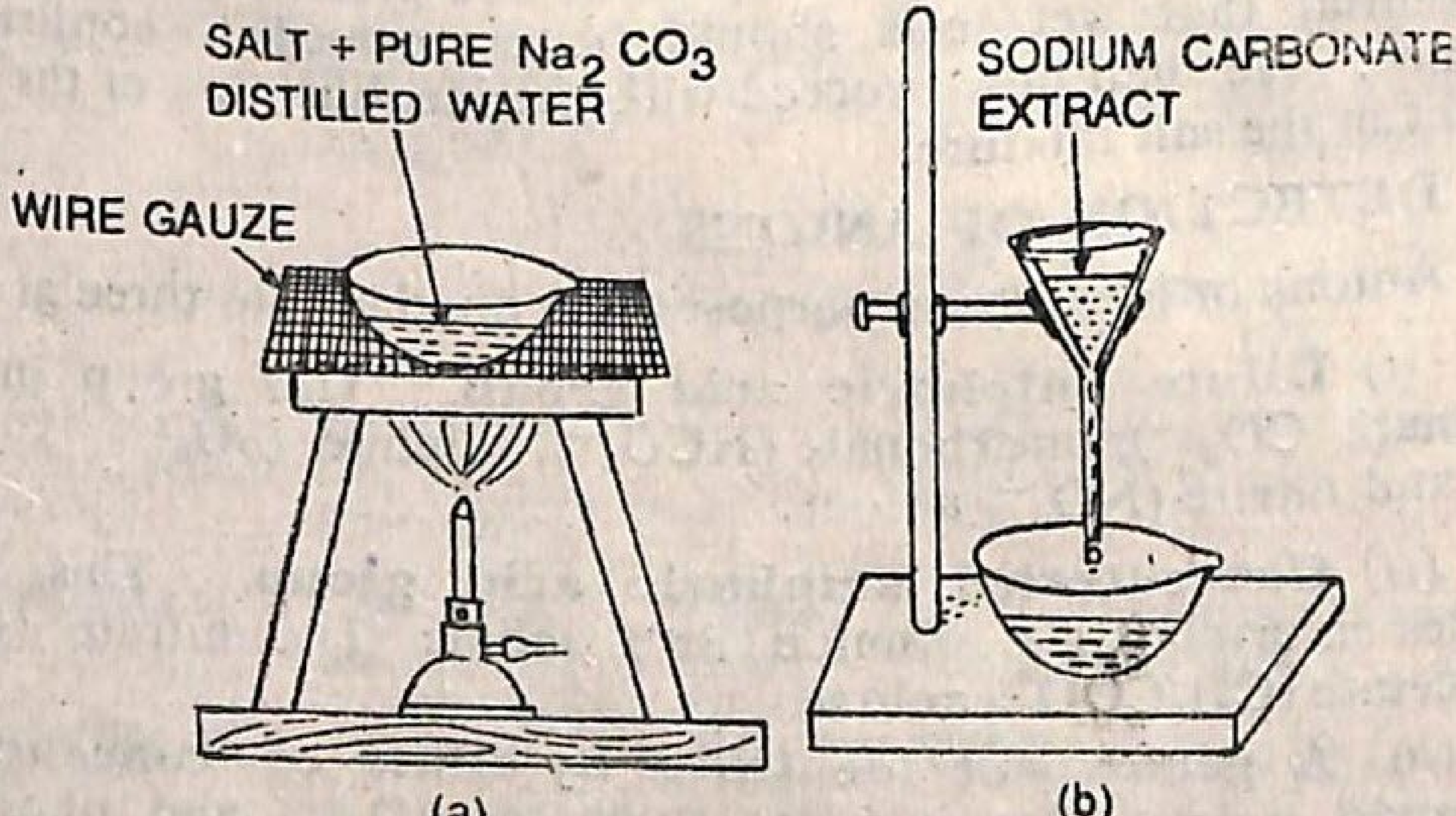


Fig. 8.4. **Preparation of sodium carbonate extract.**

Sodium carbonate extract contains an excess of unreacted sodium carbonate which interfere in the usual tests of anions. Thus, it is imperative to destroy the excess of sodium carbonate. This is accomplished by acidifying the extract. The choice of the acid depends upon the anion to be tested.

Dilute sulphuric acid group

Treat the salt/mixture with dilute sulphuric acid (Table 8.7) and observe the reaction. This treatment will help us in finding out which one of the following anions is present: (*i*) carbonate, (*ii*) bicarbonate, (*iii*) sulphide, (*iv*) sulphite, and (*v*) nitrite.

Table 8.7. Identification of CO_3^{2-}, HCO_3^-, S^{2-}, SO_3^{2-} and NO_2^-

Experiment	*Observation*	*Inference*
1. Take a little of the salt/mixture in a test tube and add dil H_2SO_4. Observe if any reaction takes place in cold. Warm gently and observe the gas.	(*i*) Brisk effervescence (due to evolution of CO_2)	CO_3^{2-} or HCO_3^- present
	(*ii*) Rotten egg smelling gas (due to evolution of H_2S)	S^{2-} present
	(*iii*) Suffocating odour of burning sulphur (due to SO_2)	SO_3^{2-} present
	(*iv*) Light brown gas with pungent odour	NO_2^- present
2. If there is brisk effervescence, pass the gas through lime water (Fig. 8.5).	Solution turns milky (due to the formation of $CaCO_3$)	CO_3^{2-} confirmed
3. If a rotten egg smelling gas evolves, bring a piece of filter paper soaked in		
(*i*) acidified lead acetate solution near the gas	Paper turns black (due to formation PbS)	S^{2-} confirned
(*ii*) acidified potassium permanganate solution near the gas	Violet colour decolourizes (due to formation of $MnSO_4$) and a yellow turbidity of S appears	S^{2-} confirmed
(*iii*) acidified potassium dichromate solution near the gas.	Acquires light green colour (due to formation of $Cr_2(SO_4)_3$ and a yellow turbidity of S appears	S^{2-} confirmed
4. To 1 mL of W.E. or S.E. add a few drops of sodium nitroprusside solution to which a few drops of alkali has been added.	Violet or purple colour due to formation of $Na_4[Fe(CN)_5NOS]$	S^{2-} confirmed

Contd.

	Experiment	Observation	Inference
5.	Acidify 1 mL of S.E. with dilute acetic acid and add 1 mL of lead acetate solution	Black ppt. (due to formation of PbS)	S^{2-} confirmed
6.	Add 0.2 g of cadmium carbonate (powder) to 2 mL of S.E. and shake well.	Yellow ppt. of CdS is obtained	S^{2-} confirmed
7.	On treating the salt/mixture with dil. H_2SO_4, if there is suffocating odour of burning sulphur (pungent gas) bring a filter paper soaked in		
	(*i*) acidified potassium permanganate solution near the gas	Violet colour decolourizes due to formation of $MnSO_4$ (colourless)	SO_3^{2-} confirmed
	(*ii*) acidified potassium dichromate solution near the gas	Orange colour turns green due to formation of $Cr_2(SO_4)_3$	SO_3^{2-} confirmed
8.	Acidify 1 mL of S.E. with dilute acetic acid, boil off CO_2 gas and now add 1 mL of $BaCl_2$ solution.	A white ppt., soluble in dilute HCl is obtained ($BaSO_3$)	SO_3^{-3} confirmed
9.	On treating the salt/mixture if brown gas evolves bring a small piece of filter paper dipped into starch+KI solution.	Paper turns blue due to the reactions of starch and I_2	NO_2^- confirmed
10.	Neutralize 1 mL of S.E. with acetic acid. Add ~0.2 g KCl+4 drops of cobalt chloride and warm.	On standing a yellow ppt. of $K_2Na[Co(NO_2)_6]$ is obtained.	NO_2^- confirmed

Distinction between carbonate and bicarbonate ions

Dissolve about 0.5 g of the salt/mixture in 4 mL of distilled water and divide it into 2 parts.

(*a*) To 1st part add a few drops of dil. HCl. A brisk effervescence due to evolution of CO_2 indicates bicabonate or carbonate.

$$Na_2CO_3+2HCl \longrightarrow H_2O+CO_2+2NaCl$$
$$NaHCO_3+HCl \longrightarrow NaCl+H_2O+CO_2$$

(*b*) To 2nd part add 0.5 mL of $MgSO_4$ solution and shake well. Formation of a white ppt. in cold confirms the presence of soluble carbonate.

$$Mg^{2+}+CO_3^{2-} \longrightarrow \underset{\text{White ppt.}}{MgCO_3\downarrow}$$

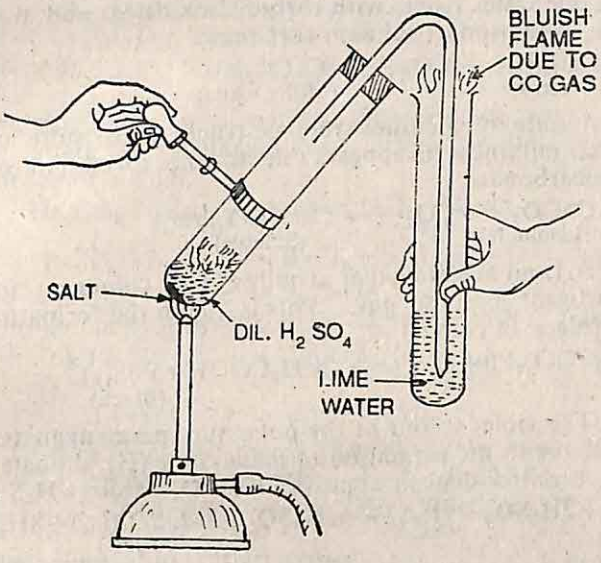


Fig. 8.5. Passing carbon dioxide through lime water.

If no ppt. appears in cold, then heat to boiling. Formation of a white ppt. confirms the presence of bicarbonate :

$$Mg^{2+} + 2HCO_3^- \longrightarrow Mg(HCO_3)_2$$

$$Mg(HCO_3)_2 \longrightarrow \underset{\text{(White ppt.)}}{MgCO_3\downarrow} + H_2O + CO_2$$

The chemistry involved in the tests performed (Table 8.7) to identify CO_3^{2-}, HCO_3^-, S^{2-}, SO_3^{2-} and NO_2^- ions is outlined below :

Reactions

1. (*i*) Carbonates and bicarbonates decompose on reacting with dilute sulphuric acid. Carbon dioxide gas evolves with brisk effervescence.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2(g)$$

$$2NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O + 2CO_2(g)$$

(*ii*) Sulphides react with dilute sulphuric acid and a rotten-egg smelling hydrogen sulphide gas evolves.

$$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S(g)$$

(*iii*) Sulphites when react with dilute H_2SO_4 give suffocating odour of burning sulphur (pungent smelling sulphur dioxide gas).

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2(g)$$

(*iv*) Nitrites react with dilute H_2SO_4 giving brown coloured NO_2 gas.

$$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + NO(g) + NO_2(g)$$

2. Lime water reacts with carbon dioxide gas and turns milky due to the formation of calcium carbonate.

$$\underset{\text{Lime water}}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\text{(Milky white)}}{CaCO_3(s)}$$

Precipitate of calcium carbonate reacts with more of carbon dioxide and milkiness disappears due to the formation of soluble calcium bicarbonate.

$$\underset{\text{(Insoluble)}}{CaCO_3(s)} + CO_2 \longrightarrow \underset{\text{(Soluble)}}{Ca(HCO_3)_2(aq)}$$

3. (*i*) Lead acetate paper acquires black colour on interacting with hydrogen sulphide gas. This is due to the formation of lead sulphide (black in colour).

$$(CH_3COO)_2Pb + H_2S \longrightarrow 2CH_3COOH + \underset{\text{(Black)}}{PbS(s)}$$

(*ii*) The violet colour of the potassium permanganate paper is discharged due to the formation of managnese (II) sulphate (colourless) and a yellow deposit appears. $KMnO_4$ oxidizes H_2S to give S.

$$\underset{\text{(Violet)}}{2KMnO_4} + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + \underset{\text{(Colourless)}}{2MnSO_4(aq)} + 8H_2O + \underset{\text{(Yellow)}}{5S(s)}$$

(*iii*) Orange coloured potassium dichromate paper acquires a green colour due to the formation of chromium (III) sulphate (green) and a yellow deposit appears. $K_2Cr_2O_7$ oxidizes H_2S to give S.

$$\underset{\text{(Orange)}}{K_2Cr_2O_7} + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + \underset{\text{(Green)}}{Cr_2(SO_4)_3(aq)} + 7H_2O + \underset{\text{(Yellow)}}{3S(s)}$$

4. Sulphides react with sodium nitroprusside forming a violet coloured complex, $Na_4[Fe(CN)_5NOS]$.

$$Na_2S + \underset{\text{Sodium nitroprusside}}{Na_2[Fe(CN_5)NO]} \longrightarrow \underset{\text{(Violet)}}{Na_4[Fe(CN)_5NOS](aq)}$$

5. Sulphides react with acidic lead acetate solution forming black precipitate of lead sulphide.

$$H_2S + (CH_3COO)_2Pb \longrightarrow 2CH_3COOH + \underset{\text{(Black)}}{PbS(s)}$$

6. Sulphides react with cadmium carbonate. A yellow precipitate of cadmium sulphide is obtained.

$$Na_2S + CdCO_3 \longrightarrow Na_2CO_3 + \underset{\text{(Yellow)}}{CdS\ (s)}$$

7. (*i*) The violet colour of potassium permanganate paper is discharged on reacting with sulphur dioxide due to the formation of manganese (II) sulphate. Sulphur dioxide acts as a reducing agent.

$$\begin{aligned} &2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5(O) \\ &5SO_2 + 5H_2O + 5(O) \longrightarrow 5H_2SO_4 \\ \hline &\underset{\text{(Violet)}}{2KMnO_4} + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2H_2SO_4 + \underset{\text{(Colourless)}}{2MnSO_4} \end{aligned}$$

(*ii*) Orange coloured potassium dichromate paper acquires a light green colour on reacting with sulphur dioxide and due to the formation of $Cr_2(SO_4)_3$. Sulphur dioxide acts as an reducing agent.

$$\underset{\text{(Orange)}}{K_2Cr_2O_7}+H_2SO_4+3SO_2 \longrightarrow K_2SO_4+H_2O+\underset{\text{(Green)}}{Cr_2(SO_4)_3}$$

8. Sulphites react with barium chloride solution forming a white precipitate of barium sulphite. Barium sulphite is soluble in dilute hydrochloric acid.

$$Na_2CO_3+BaCl_2 \longrightarrow 2NaCl+\underset{\text{(White)}}{BaSO_3\,(s)}$$

$$BaSO_3+2HCl \longrightarrow BaCl_2+H_2O+SO_2$$

9. Starch-iodide paper turns blue due to the liberation of iodine from iodide by nitrous acid which reacts with starch.

$$KI+\underset{\text{(From } NO_2^-)}{2HNO_2} \longrightarrow 2H_2O+2NO+I_2$$

$$I_2+\text{Starch} \longrightarrow \text{Blue colouration}$$

10. Nitrites react with cobalt chloride in the presence of acetic acid. A yellow crystalline precitate of $K_2\,Na[Co(NO_2)_6]$ is formed,

$$6NaNO_2+2KCl+CoCl_3 \longrightarrow \underset{\text{(Yellow)}}{K_2Na[Co(NO_2)_6](s)}+5NaCl$$

Concentrated sulphuric acid group

Take about 0·5 g of the solid salt or mixture in a dry test-tube, add about 1 mL of conc. H_2SO_4. Warm the contents (do not boil). Look for the presence of : (*i*) chloride, Cl^-, (*ii*) bromide, Br^-, (*iii*) iodide, I^-, (*iv*) nitrate, NO_3^- and acetate, CH_3COO^-.

Table 8.8. Identification of Cl^-, Br^-, I^-, NO_3^- and CH_3COO^-

Experiment	*Observation*	*Inference*
1. Take a small quantity of the salt/mixture in a test-tube and add conc. H_2SO_4. Observe if any reaction takes place in cold. Warm gently and observe the gas evolved.	(*i*) Pungent smelling and irritating gas (due to evolution of HCl)	Cl^- present
	(*ii*) Reddish brown fumes evolves (may be due to HBr and Br_2)	Br^- present
	(*iii*) Violet vapours	I^- present
	(*iv*) Light brown fumes with a characteristic irritating smell (due to NO_2 gas)	NO_3^- present
	(*v*) Vinegar smell	CH_3COO^- present
2. If a pungent smelling gas evolves		
(*i*) Bring a glass rod carrying a drop of ammonia solution near the issuing gas (Fig. 8.6)	Dense white fumes of NH_4Cl are produced	Cl^- present

Contd.

Experiment	*Observation*	*Inference*
(*ii*) Add a small amount of MnO_2 to the reaction mixture and heat it.	Greenish yellow Cl_2 gas evolves. It has a pungent odour.	Cl^- present
(*iii*) Bring moist iodized starch-paper near the opening of the test-tube in (*ii*).	Dark blue colour appears.	Cl^- present
3. (*i*) Acidify 1 mL of W.E. or S.E. with dilute HNO_3 and add $AgNO_3$ solution.	Dirty white ppt. of AgCl appears which turns grey on getting exposed to light.	Cl^- confirmed
(*ii*) Add aqueous ammonia to the white ppt of AgCl.	ppt. dissolves forming a soluble complex	Cl^- confirmed
4. **Chromyl Chloride Test:** Take a smare amount of mixture salt (1 part) and $K_2Cr_2O_7$ (1 part) in a test tube. Add conc. H_2SO_4 and heat.	Red vapours of chromyl chloride are produced.	Cl^- confirmed
Pass the red vapours of CrO_2Cl_2 through dil. NaOH solution.	Yellow solution of sodium chromate is obtained.	Cl^- confirmed
Acidify the yellow solution with acetic acid and add lead acetate solution.	Yellow ppt. of lead chromate is obtained	Cl^- confirmed
5. If a salt/mixture on treating with conc H_2SO_4 produces brown fumes of HBr and Br_2		
(*i*) add a small quantity of MnO_2 to the reaction mixture and heat it	Dark brown fumes of Br_2 evolve	Br^- present
(*ii*) Expose a starch paper to the issuing fumes	Starch paper turns yellow	Br^- present
6. (*i*) Acidify 1 mL of W.E. or S.E. with dilute HNO_3 and add $AgNO_3$ solution	Light yellow curdid ppt. of AgBr	Br^- confirmed
(*ii*) Add aqueous ammonia solution to the yellow ppt.	Sparingly soluble in ammonia solution	Br^- confirmed
7. Acidify 1 mL of W.E. or S.E. with dilute H_2SO_4. Add 2 mL of an organic solvent (CS_2, $CHCl_3$, CCl_4 or benzene) followed by chlorine water. Shake the tube well.	Organic layer acquires yellow, red or brown colour depending on the concentration of Br_2 and on the solvent	Br^- confirmed
8. If a salt/mixture on treating with conc. H_2SO_4 produces violet vapours of iodine		
(*i*) Add a small amount of MnO_2 to reaction mixture and heat	Dense violet vapours evolve	I^- present
(*ii*) Expose a starch paper to the issuing vapours.	Starch paper turns blue.	I^- confirmed
9. (*i*) Acidify 1 mL of W.E. or S.E. with dilute HNO_3 and add $AgNO_3$ solution.	Yellow curdid ppt. of AgI	I^- confirmed

Contd.

Experiment	*Observation*	*Inference*
(*ii*) Add aqueous ammonia solution to the yellow ppt.	Insoluble in aqueous ammonia	I^- confirmed.
10. Acidify 1 mL of W.E. or S.E. with dilute H_2SO_4. Add 2 mL of an organic solvent (CS_2, $CHCl_3$, CCl_4 or benzene) and about 1 mL of chlorine water. Shake well.	Organic layer extracts iodine and becomes red-violet.	I^- confirmed.
11. If a salt on reacting with conc. H_2SO_4 produces light brown fumes.		
(*i*) Add copper turnings to the reaction mixture and heat.	Dense brown fumes evolve	No_3^- present
(*ii*) Expose a moist potassium iodide paper to the issuing fumes	The paper acquires yellow colour	NO_3^- present
(*iii*) Expose a moist iodized starch paper to the issuing fumes.	The paper acquires a blue colour	NO_3^- present
12. To W.E. add freshly prepared ferrous sulphate solution followed by conc. H_2SO_4 along the side of the tube.	Conc. H_2SO_4 forms the bottom layer. A brown ring appears at the junction of the two liquids due to the formation of complex.	NO_3^- confirmed.
13. If a salt/mixture on reacting with conc. H_2SO_4 gives vinegar smell, add a few mL of ethyl alcohol	Pleasant odour	CH_3COO^- present
14. To W.E. add neutral ferric chloride solution	Blood red coloured solution	CH_3COO^- confirmed
Heat the blood-red coloured solution	A red brown ppt. of basic acetate is precipitated	CH_3COO^- confirmed

The chemistry involved in the tests performed (Table 8.8) to identify Cl^-, Br^-, I^-, NO_3^- and CH_3COO^- is outlined below :

Reactions. 1. (*i*) Chlorides react when heated with conc. H_2SO_4. A pungent smelling and irritating gas evolves.

$$NaCl+H_2SO_4 \longrightarrow NaHSO_4+\underset{\text{Hydrogen chloride}}{HCl\,(g)}$$

(*ii*) Bromides react when heated with conc. H_2SO_4. Reddish brown fumes evolve with a penetrating odour of a mixture of hydrogen bromide and bromine. SO_2 is also produced as HBr produced in reaction acts as reducing agent.

$$NaBr+H_2SO_4 \longrightarrow NaHSO_4+\underset{\text{Hydrogen bromide}}{HBr\,(g)}$$

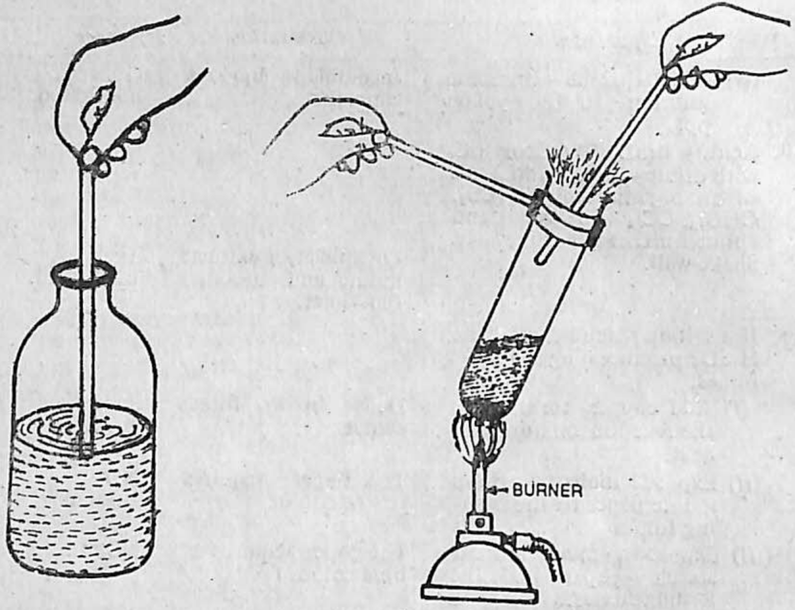


Fig. 8.6. Testing the issuing gas with reagent-dipped glass rod

$$2HBr + H_2SO_4 \longrightarrow Br_2\,(g) + \underset{\text{Sulphur dioxide}}{SO_2(g)} + 2H_2O$$

(*iii*) **Iodides** react when heated with conc. H_2SO_4. Dense violet vopours evolve. Some hydrogen iodide gas also forms which reduces H_2SO_4 to SO_2, H_2S and S.

$$NaI + H_2SO_4 \longrightarrow NaHSO_4 + \underset{\text{Hydrogen iodide}}{HI\,(g)}$$

$$2HI + H_2SO_4 \longrightarrow 2H_2O + I_2(g) + \underset{\text{Sulphur dioxide}}{SO_2\,(g)}$$

$$6HI + H_2SO_4 \longrightarrow 3I_2 + \underset{\text{Sulphur}}{S\,(s)} + 4H_2O$$

$$8HI + H_2SO_4 \longrightarrow 4I_2 + \underset{\text{Hydrogen sulphide}}{H_2S\,(g)} + 4H_2O$$

(*iv*) Nitrates react when heated with conc H_2SO_4. Irritating brown fumes of nitrogen dioxide evolve.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

$$4HNO_3 \longrightarrow 2H_2O + O_2 + \underset{\text{Nitrogen dioxide}}{4NO_2\,(g)}$$

(*v*) Acetates react when heated with conc. H_2SO_4. Acetic acid is formed which smells like vinegar.

$$2NaOOCCH_3 + H_2SO_4 \longrightarrow 2CH_3COOH + Na_2SO_4$$

2. (*i*) Aqueous ammonia reacts with hydrogen chloride gas forming dense white fumes of ammonium chloride.

$$NH_3 + HCl \longrightarrow \underset{\text{(Dense white fumes)}}{NH_4Cl\,(g)}$$

(*ii*) Manganese dioxide oxidizes hydrogen chloride to chlorine gas (greenish yellow).

$$MnO_2+4HCl \longrightarrow MnCl_2+2H_2O+\underset{\text{(Greenish yellow)}}{Cl_2\ (g)}$$

(*iii*) In the presence of Cl_2 iodine vapours are produced which in turn, react with starch paper imparting dark blue colour.

$$2KI+Cl_2 \longrightarrow 2KCl+I_2\ (g)$$

3. (*i*) Solution of chlorides react with silver nitrate forming a dirty white precipitate of silver chloride. It turns grey on getting exposed to light.

$$NaCl+AgNO_3 \longrightarrow NaNO_3+\underset{\text{(Dirty white)}}{AgCl\ (s)}$$

(*ii*) The ppt. of AgCl dissolves in aqueous ammonia forming a soluble complex, $[Ag(NH_3)_2]Cl$.

$$AgCl+2NH_3 \longrightarrow \underset{\text{Diammine silver chloride}}{[Ag(NH_3)_2]Cl\ (aq)}$$

4. A mixture of chloride and potassinm dichromate with conc. H_2SO_4 gives red vapours of chromyl chloride, CrO_2Cl_2.

$$4NaCl+K_2Cr_2O_7+3H_2SO_4 \xrightarrow{\text{Heat}} K_2SO_4+2Na_2SO_4+3H_2O+\underset{\substack{\text{(Red vapours)}\\ \text{Chromyl chloride}}}{2CrO_2Cl_2(g)}$$

Red vapours of CrO_2Cl_2, when passed through a solution of sodium hydroxide, react to form a yellow solution of sodium chromate.

$$CrO_2Cl_2+4NaOH \longrightarrow 2NaCl+2H_2O+\underset{\text{Sodium chromate}}{Na_2CrO_4}$$

Sodium chromate reacts with lead acetate in the presence of acetic acid to give a yellow precipitate of lead chromate.

$$Na_2CrO_4+(CH_3COO)_2Pb \longrightarrow CH_3COONa+\underset{\substack{\text{(Yellow)}\\ \text{Lead chromate}}}{PbCrO_4\ (s)}$$

5. (*i*) Manganese dioxide oxidizes hydrogen bromide gas to bromine vapours.

$$MnO_2+2HBr+H_2SO_4 \longrightarrow MnSO_4+2H_2O+\underset{\text{(Brown)}}{Br_2\ (g)}$$

(*ii*) Bromine vapours react with starch forming a yellow coloured complex, hence, the paper becomes yellow.

6. (*i*) Solution of bromides react with silver nitrate forming a light yellow curdid ppt. of silver bromide.

$$NaBr+AgNO_3 \longrightarrow NaNO_3+\underset{\text{(Light yellow)}}{AgBr}$$

(*ii*) The ppt. of AgBr is sparingly soluble in aqueous ammonia solution, forming a soluble complex $[Ag(NH_3)_2]Br$.

7. Chlorine water oxidizes bromides to bromine. Organic solvent extracts the liberated bromine and acquires a yellow orange

colour depending upon the concentration of bromine and on the solvent.

$$2NaBr + CCl_2 \longrightarrow 2NaCl + \underset{\text{(Soluble in organic solvent)}}{Br_2}$$

8. (*i*) Hydrogen iodide is readily oxidized to iodine by manganese dioxide when more of violet vapours of iodine evolve.

$$MnO_2 + 2HI + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + \underset{\text{(Violet)}}{I_2(g)}$$

(*ii*) Iodine vapours react with starch forming a blue coloured complex ; hence the paper becomes blue.

9. (*i*) Solution of iodides react with siver nitrate to give a yellow curdid precipitate of silver iodide.

$$NaI + AgNO_3 \longrightarrow NaNO_3 + \underset{\text{(Yellow)}}{AgI(s)}$$

(*ii*) The precipitate of AgI is insoluble in aqueous ammonia.

10. Chlorine water oxidizes iodides to iodine. O ganic solvent extracts the liberated iodine and acquires red violet colour.

$$2NaI + Cl_2 \longrightarrow 2NaCl + \underset{\text{(Soluble in organic solvent)}}{I_2}$$

11. (*i*) Copper turnings react with nitric acid produced in the reaction mixture forming more of nitrogen dioxide, hence the dense brown fumes.

$$NaNO_3 + H_2SO_4 \longrightarrow HNO_3 + NaHSO_4$$

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2H_2O + \underset{\substack{\text{(Brown)}\\ \text{Nitrogen dioxide}}}{2NO_2(g)}$$

(*ii*) Iodine liberates during the reaction and the paper absorbs iodine which imparts yellow colour.

$$NO_2 + 2KI + H_2O \longrightarrow 2KOH + NO + I_2(g)$$

(*iii*) Iodine liberates during the reaction and it interacts with starch forming a blue coloured complex.

12. Nitrates react with ferrous sulphate in the presence of conc. H_2SO_4. A brown ring appears at the junction of the two liquid layers (Fig. 8.7).

Ferrous sulphate, at first, reduces the nitrate to nitrite and then to nitric oxide. This oxide coordinates to the unoxidized portion of ferrous sulphate.

$$NO_3^- + H^+ \longrightarrow HNO_3$$

$$2HNO_3 + 3H_2SO_3 + 6FeSO_4 \longrightarrow 3Fe_2(SO_4)_2 + 2NO + 4H_2O$$

$$FeSO_4 + 5H_2O + NO \longrightarrow \underset{\text{(Brown ring)}}{[Fe(H_2O)_5NO]SO_4}$$

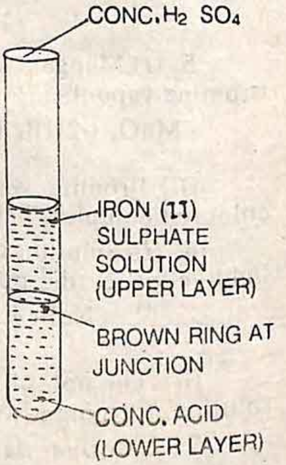


Fig. 8.7. Brown ring test for nitrate.

13. Acetic acid and its salt under the action of ethyl alcohol in the presence of sulphuric acid, form ethyl acetate which is detected by its pleasant odour.

$$CH_3COOH+HOC_2H_5 \overset{H_2SO_4}{\rightleftharpoons} CH_3COOC_2H_5+H_2O$$

14. Ferric salts with acetate ions form ferric acetate which is recognized by its blood-red colour.

$$3CH_3COONa+FeCl_3 \longrightarrow \underset{\text{(Blood-red)}}{(CH_3COO)_3Fe}+3NaCl$$

On dilution and heating, basic acetate is precipitated.

$$(CH_3COO)_3Fe+2H_2O \longrightarrow \underset{\text{Basic acetate}}{[CH_3COO(OH)_2]Fe(s)}+2CH_3COOH$$

Tests for anions not identified by dilute or concentrated H_2SO_4.

Anions which cannot be identified on reacting with dilute or conc. H_2SO_4, are listed below :

(*i*) Sulphate, SO_4^{2-} ; and (*ii*) phosphate ; PO_4^{3-}.

Such anions are identified and thus confirmed by using sodium carbonate extract only. Some other tests can also be performed.

Proceed as given in Table 8.9.

Table 8.9. Identification of SO_4^{2-} and PO_4^{3-}

Experiment	*Observation*	*Inference*
1. Acidify 2-3 mL of W.E. or S.E. with dil. HCl and divide the solution in two parts.		
(*i*) To one part add barium chloride solution.	White ppt. of $BaSO_4$ is obtained. Insoluble in all mineral acids.	SO_4^{2-} confirmed
(*ii*) To the other part of the solution add acetic acid and lead acetate solution.	White ppt. of lead sulphate is obtained which is soluble in ammonium acetate solution, due to the formation of soluble lead acetate.	SO_4^{2-} confirmed
2. Acidify 2-3 mL of S.E. with dil. HNO_3. To this add 2-3 mL of conc. HNO_3 and 5 mL of ammonium molybdate solution. Now heat the contents.	Slow formation of canary-yellow ppt. of ammonium phosphomolybdate takes place.	PO_4^{3-} present

The chemistry involved in the tests performed (Table 8.9) to identify SO_4^{2-} and PO_4^{3-} is outlined below :

Reactions

1. (*i*) Solutions of sulphates react with barium chloride and form a white precipitate of barium sulphate which is insoluble in all mineral acids.

$$Na_2SO_4+BaCl_2 \longrightarrow 2NaCl+\underset{\text{(White)}}{BaSO_4\ (s)}$$

(*ii*) Solution of sulphates react with lead acetate and form a white precipitate of lead sulphate.

$$Na_2SO_4+(CH_3COO)_2Pb \longrightarrow 2CH_3COONa+\underset{\text{(White)}}{PbSO_4(s)}$$

Precipitate of lead sulphate dissolves in ammonium acetate solution due to the formation of soluble lead acetate.

$$PbSO_4+2CH_3COONH_4 \longrightarrow NH_4)_2SO_4+\underset{\text{Lead acetate}}{(CH_3COO)_2Pb}$$

2. Solutions of phosphates react with ammonium molybdate in the presence of concentrated nitric acid to yield a canary-yellow precipitate of ammonium phosphomolybdate.

$$Na_2HPO_4+12(NH_4)_2MoO_4+23HNO_3 \longrightarrow \underset{\text{(Canary yellow)}}{(NH_4)_3[PMo_{12}O_{40}](s)}$$
$$+2NaNO_3+12NH_4NO_3+12H_2O$$

8.5. DETECTION OF CATIONS

Cations are divided into analytical groups. The classification of the cations into analytical groups is based on the solubility of some salts which they form on reacting with reagents. All cations have been divided into six analyticaly groups on the basis of the difference in solubilities of their chlorides, sulphides, hydroxides and carbonates under different conditions of acidity and alkalinity (Table 8.10). The reagent used to precipitate the specific group is known as a group reagent.

Table 8.10. Classification of cations into groups

Group	*Group reagent*	*Cation*
I	Dilute HCl	Pb^{2+} and Hg_2^{2+}(precipitated as chlorides)
II	H_2S in acidic medium (HCl)	Hg^{2+}, Cu^{2+}, Cd^{2+} As^{3+} and Sb^{3+} (precipitated as sulphides)
III	NH_4OH in the prssence of NH_4Cl	Fe^{2+}, Fe^{3+} and Al^{3+} (recipitated as hydroxides)
IV	H_2S in alkaline medium (NH_4OH)	Ni^{2+}, Zn^{2+}, Mn^{2+} and Co^{2+} (precipitated as sulphides)
V	$(NH_4)_2CO_3$ in alkaline medium (NH_4OH)	Ca^{2+}, Ba^{2+} and Sr^{2+} (precipitated as carbonates)
VI	No common reagent	Mg^{2+}, NH_4^+, and K^+ (NH_4^+ ion included in zero group)

Preparation of original solution. Most of the reactions used in qualitative analysis occur in aqueous solution. Thus, the first step in the systematic analysis of cations is to prepare a clear (colourless or coloured) salt/mixture solution (called **original solution**, O S.). For this purpose, take about 0·1 g of the salt/mixture and try to dissolve it in about 2 mL of

(*i*) distilled water (cold or hot),

(*ii*) dilute hydrochloric acid (cold or hot), or

(*iii*) concentrated hydrochloric acid (cold or hot).

The solvents listed above should be tried one by one in the given order. After selecting the suitable solvent, prepare the O.S. by dissolving about 1 g of the salt in 10-15 mL of the solvent.

Notes. (*i*) For the preparation of O.S. first try to dissolve the salt/mixture in a cold solvent (water, dilute hydrochloric acid (or concentrated hydrochloric acid). If it does not dissolve, heat it. In such a case, cool the solution and see if the salt/mixture separates out or not. If it does, try the next solvent.

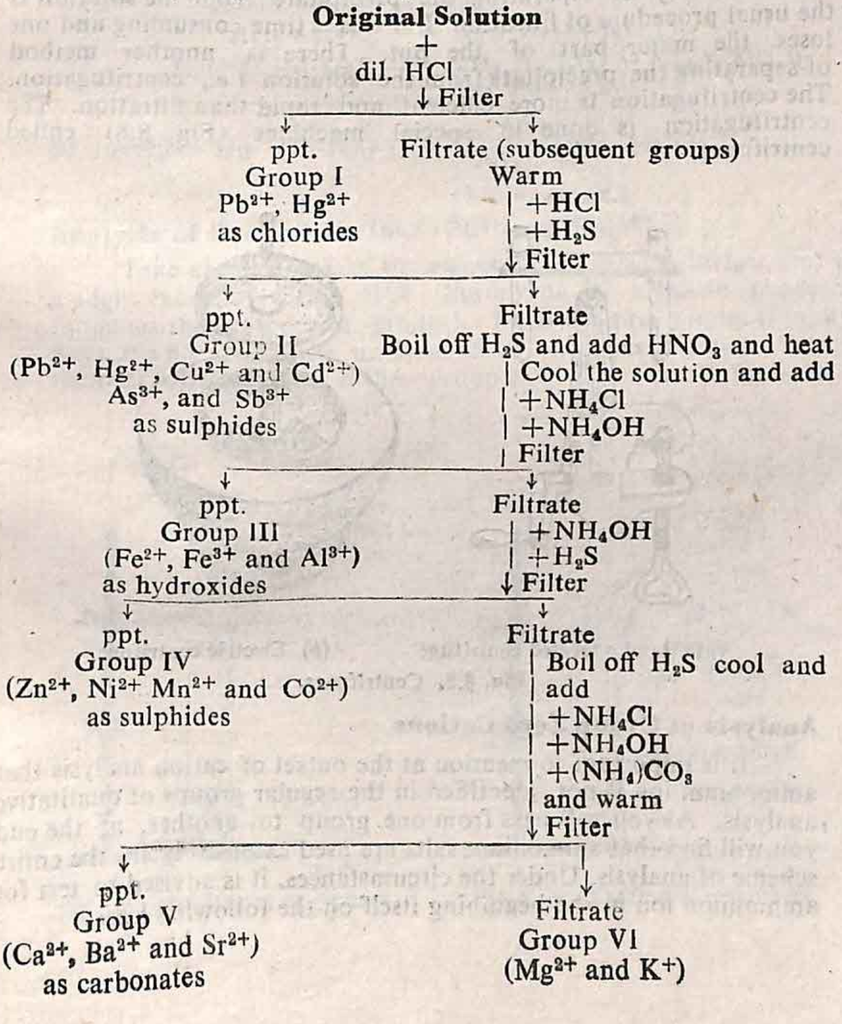
(*ii*) If the solution is prepared in concentrated hydrochloric acid, it should be diluted before proceeding with the cation analysis.

(*iii*) The effect of the solvent on the salt/mixture should be for a sufficient period.

(*iv*) The least quantity of the acid should be used for the preparation of original solution.

(*v*) At this level, it is advised not to employ HNO_3 and H_2SO_4 as solvent, as they interfere in the usual analysis. Sulphuric acid precipitates Ba^{2+}, Sr^{2+}, Ca^{2+} and Pb^{2+} as their sulphates and thus salt/mixture containing these cations will never dissolve.

The classification and separation of all the six groups on the basis of group reagents is portrayed in the flow chart.



Original Solution
+
dil. HCl
↓ Filter

ppt.
Group I
Pb^{2+}, Hg^{2+}
as chlorides

Filtrate (subsequent groups)
Warm
| +HCl
| $+H_2S$
↓ Filter

ppt.
Group II
(Pb^{2+}, Hg^{2+}, Cu^{2+} and Cd^{2+})
As^{3+}, and Sb^{3+}
as sulphides

Filtrate
Boil off H_2S and add HNO_3 and heat
| Cool the solution and add
| $+NH_4Cl$
| $+NH_4OH$
| Filter

ppt.
Group III
(Fe^{2+}, Fe^{3+} and Al^{3+})
as hydroxides

Filtrate
| $+NH_4OH$
| $+H_2S$
↓ Filter

ppt.
Group IV
(Zn^{2+}, Ni^{2+} Mn^{2+} and Co^{2+})
as sulphides

Filtrate
| Boil off H_2S cool and add
| $+NH_4Cl$
| $+NH_4OH$
| $+(NH_4)CO_3$
| and warm
↓ Filter

ppt.
Group V
(Ca^{2+}, Ba^{2+} and Sr^{2+})
as carbonates

Filtrate
Group VI
(Mg^{2+} and K^+)

Notes. 1. Test the presence of various cations systematically. Don't skip any group.

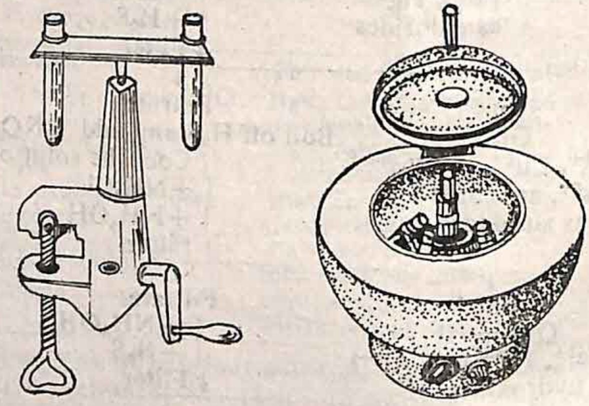
2. It is important to ensure the absence of one group before starting the analysis of next group.

3. Excessive dilution should be avoided. As one reaches group V, the bulk of the solution is difficult to handle and the concentration of individual ions becomes too low. In the process, at times one misses the detection of group V cations.

It is advised to concentrate the solution at the outset of each group. Don't through the solution into the sink.

4. The precipitates of a group should be filtered and washed carefully.

One way of separating the precipitate from the solution is the usual procedure of filtration. But this is time consuming and one loses the major part of the ppt. There is another method of separating the precipitate from the solution *i.e.*, centrifugation. The centrifugation is more efficient and rapid than filtration. The centrifugation is done in special machines (**Fig**. 8.8) called centrifuges.



(*a*) Hand operated centrifuge (*b*) Electric centrifuge

Fig. 8.8. Centrifuges.

Analysis of Group Zero Cations

It is important to mention at the outset of cation analysis that ammonium ion is not identified in the regular groups of qualitative analysis. As you will pass from one group to another, at the end you will find that ammonium salts are used extensively in the entire scheme of analysis. Under the circumstances, it is advised to test for ammonium ion in the beginning itself on the following lines.

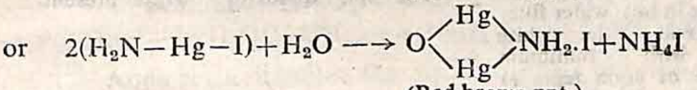
Heat 0.5 g of the mixture in a test tube with about 2 mL of sodium hydroxide solution. Evolution of NH_3 gas indicates the presence of NH_4^+ radical.

The ammonia gas can either be detected by its odour or bringing a glass rod dipped into HCl near the exit of gas. The interaction of gas with HCl gives dense white fumes due to the formation of NH_4Cl.

$$NH_4^+ (s) + OH^-(aq) \xrightarrow{\text{Heat}} NH_3 (g) + H_2O(l)$$
$$NH_3 (g) + HCl (l) \longrightarrow NH_4Cl(g)$$

Ammonia gas when passed through Nessler's reagent solution gives a brown ppt. of iodide of Millon's base. This also confirms the presence of NH_4^+ ion in the mixture.

$$NH_4^+ + NaOH \longrightarrow NH_3 + H_2O + Na^+$$
$$\underset{\text{Nessler's reagent}}{K_2HgI_4} \longrightarrow 2KI + HgI_2$$
$$HgI_2 + 2NH_3 \longrightarrow Hg(NH_2)I + NH_4I$$
$$Hg(NH_2)I + HgI_2 \longrightarrow \underset{\text{(Red brown ppt.)}}{NH_2\ Hg_2I_3(s) \text{ or } [Hg_2I_2\ NH_2]I}$$



$$\text{or}\quad 2(H_2N-Hg-I) + H_2O \longrightarrow O\langle{}^{Hg}_{Hg}\rangle NH_2.I + NH_4I$$

(Red brown ppt.)

Analysis of Group I Cations (Pb^{2+} and Hg_2^{2+})

Take about 10 mL of the **aqueous original solution,** and add a slight excess of dilute HCl. Formation of a white precipitate indicates the presence of group I. Filter the precipitate (Fig. 8.9). Keep the filtrate for the analysis of the subsequent groups. Analyse the ppt. for the cations of first group as given in the Table 8.11.

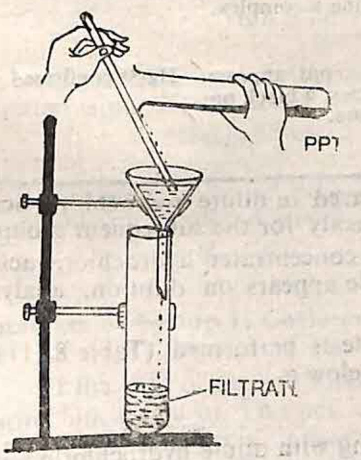


Fig. 8.9. Fitration of precipitate

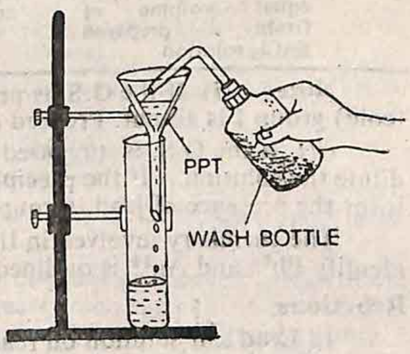


Fig. 8.10. Washing of precipitate

Table 8.11. Analysis of group I cations (Pb^{2+} and Hg^{2+})

Experiment	*Observation*	*Inference*
1. Wash the ppt. (Fig. 8·10) and add 2-3 ml of distilled water to the white ppt. and heat Divide the hot solution in fours parts.	The ppt. dissolves	Pb^{2+} present
(*i*) Cool one part under tap water.	(*i*) White ppt. of $PbCl_2$ separates out.	Pb^{2+} confirmed
(*ii*) To the second part of hot solution add potassium chromate solution.	(*ii*) Yellow ppt. of $PbCrO_4$ appears.	Pb^{2+} confirmed
(*iii*) To the third part of hot solution add potassium iodide solution.	(*iii*) Yellow ppt. of PbI_2 appears.	Pb^{2+} confirmed
(*iv*) To the fourth part of the hot solution add dilute H_2SO_4 and a few drops of alcohol.	(*iv*) White ppt. of $PbSO_4$ appears.	Pb^{2+} confirmed
2. If the white ppt. does not dissolve in hot water filter and treat the white ppt. with minimum volume of aqua regia (1 part conc. HNO_3 and 3 parts conc. HCl) Heat to dryness. Treat the solid mass with water. Divide the solution in two parts.	The ppt. dissolves	Hg_2^{2+} present
(*i*) To one part of the solution add KI solution	Red ppt. of HgI_2 appears	Hg_2^{2+} confirmed
(The reaction should be carried out at $pH \geqslant 7$) Add excess of KI solution	Red ppt. dissolves forming a complex.	
(*ii*) To the other part of the solution add an equal volume of freshly prepared $SnCl_2$ solution	A white ppt. appears. At times, a black ppt. appears.	Hg_2^{2+} confirmed

Notes. (*i*) If the O.S. is prepared in dilute hydrochloric acid (cold) group I is absent. Proceed directly for the subsequent groups.

(*ii*) If the O.S. is prepared in concentrated hydrochloric acid, dilute the solution. If the precipitate appears on dilution, analyse it for the presence of lead (Group I).

The chemistry involved in the tests performed (Table 8.11) to identify Pb^{2+} and Ag^{2+} is outlined below :

Reactions

1. Lead salt solution on reacting with dilute hydrochloric acid forms white precipitate of lead chloride which is soluble in hot water.

$$Pb^{2+} + 2HCl \longrightarrow \underset{\text{(white)}}{PbCl_2 \downarrow} + 2H^+$$

(*i*) Lead chloride appears on cooling the solution under tap water.

(*ii*) Lead salt solution reacts with potassium chromate to give yellow ppt of lead chromate.

$$\underset{\text{(Soluble in hot water)}}{PbCl_2(aq) + K_2CrO_4} \longrightarrow \underset{\text{(Yellow)}}{PbCrO_4\,(s)} + 2KCl$$

(*iii*) Potassium iodide reacts with lead chloride solution forming a yellow ppt. of lead iodide.

$$PbCl_2\,(aq) + 2KI \longrightarrow 2KCl + \underset{\text{(Yellow)}}{PbI_2\,(s)}$$

The precipitate of lead iodide is soluble in hot solution, which reappears on cooling with a distinct shine.

(*iv*) Sulphate ions react with lead salt solution and form white ppt. (alcohol reduces the solubility of the ppt.) which is soluble in ammonium acetate solution

$$PbCl_2\,(aq) + H_2SO_4 \longrightarrow PbSO_4\,(s) + 2HCl$$

$$PbSO_4(s) + 2NH_4OOCCH_3 \longrightarrow (NH_4)_2SO_4 + Pb(OOCCH_3)_2(aq)$$

(2) Aqua regia dissolves the ppt. forming soluble mercuric chloride.

$$Hg_2Cl_2 + 2HNO_3 + 6HCl \longrightarrow 2HgCl_2 + 2NaCl + 4H_2O + Cl_2$$

(*i*) Mercury salt solution reacts with KI solution. A red ppt. of HgI_2 appears.

$$Hg^{2+} + 2I^- \longrightarrow \underset{\text{(Red)}}{HgI_2\,(s)}$$

The red ppt. dissolves in the presence of excess reagent.

$$HgI_2 + 2I^- \longrightarrow \underset{\text{(Soluble)}}{[HgI_4]^{2-}}$$

(*ii*) Addition of $SnCl_2$ reduces $HgCl_2$ to white Hg_2Cl_2. The reaction is possible in acidic solution.

$$2HgCl_2 + SnCl_2 \longrightarrow \underset{\text{(White)}}{Hg_2Cl_2(s)} + SnCl_4$$

Further addition of $SnCl_2$ reduces white Hg_2Cl_2 to a black precipitate of metallic mercury

$$SnCl_2 + Hg_2Cl_2 \longrightarrow \underset{\text{(Black)}}{2Hg(s)} + SnCl_4$$

Analysis of Group II Cations (Pb^{2+}, Hg^{2+}, Cd^{2+}, Cu^{2+}, As^{3+} and Sb^{3+})

If the O.S. of the salt/mixture does not give any ppt. with dilute hydrochloric acid or if no ppt. appears when the O.S. is prepared in dilute hydrochloric acid, it means group I is absent. In case group I is present there, the filtrate is used for group 2 cations.

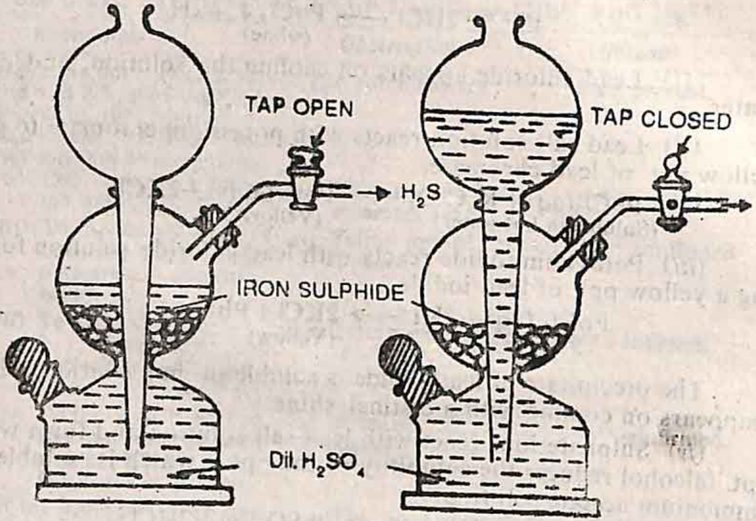


Fig. 8.11. Kipp's apparatus for the continuous supply of H_2S gas.

Now warm this acidified O.S. or filtrate from group I as the case may be and pass hydrogen sulphide gas from the Kipp's apparatus (Fig. 8.11) through the solution. If a coloured ppt. (black, yellow or orange) is obtained the group II appears to be present. A black ppt. shows the presence of Pb^{2+}, Hg^{2+} or Cu^{2+}, a yellow ppt. shows Cd^{2+} or As^{3+} and a orange, ppt shows Sb^{3+}. It is advisable to pass H_2S gas through a few mL of O.S. or filtrate initially. If there is ppt. then pass H_2S gas through the remaining solution also. If there is no ppt. then store this solution.

Now separate the ppt. by filtration and reject the filtrate.

$$Pb^{2+} + H_2S \longrightarrow \underset{\text{(Black)}}{PbS\,(s)} + 2H^+$$

$$Hg^{2+} + H_2S \longrightarrow \underset{\text{(Black)}}{HgS(s)} + 2H^+$$

$$Cu^{2+} + H_2S \longrightarrow \underset{\text{(Black)}}{CuS(s)} + 2H^+$$

$$Cd^{2+} + H_2S \longrightarrow \underset{\text{(Yellow)}}{CdS(s)} + 2H^+$$

(Possible in very dilute solution only)

$$2As^{3+} + 3H_2S \longrightarrow \underset{\text{(Yellow)}}{As_2S_3(s)} + 6H^+$$

$$2Sb^{3+} + 3H_2S \longrightarrow \underset{\text{(Orange)}}{Sb_2S_3(s)} + 6H^+$$

Table 8·12. Analysis of group II cations (Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, As^{3+} and Sb^{3+})

Wash the ppt. with hot distilled water and reject the washings. Take the washed ppt. in a test tube (Fig. 8.12).

Experiment	Observation	Inference
Black ppt		
1. Treat the washed back ppt. with 3 4 mL of 50% HNO_3 and boil	A colourless or blue coloured solution is obtained	Pb^{2+} or Cu^{2+} indicated
2. To the colourless solution (From test 1) add 1 mL of alcohol and a few mL of dil H_2SO_4	White ppt. (due to $PbSO_4$)	Pb^{2+} present
To the white ppt. add ammonium acetate solution.	$PbSO_4$ is soluble in ammonium acetate solution	Pb^{2+} present
Note. Divide the solution in two parts and perform the tests with K_2CrO_4, and KI as given in Table 8.11.		
3. To the blue solution (From test 1) add an excess of aqueous ammonia solution.	A deep blue solution of $[Cu(NH_3)_4(NO_3)_2]$ is obtained.	Cu^{2+} confirmed
4. To the O.S. (or the solution obtained in test no. 3) add potassium ferrocyanide solution.	Reddish brown ppt. of $Cu_2[Fe(CN)_6]$ appears.	Cu^{2+} confirmed
5. Treat the black residue (from test 1) with aqua regia. Heat to almost dryness. Extract the solid mass in distilled water. Divide the solution in three parts.		
Note. Perform the test with KI and $SnCl_2$ as given in Table 8.11.		
To the third part add Cu turnings.	Grey deposit is seen on Cu	Hg^{2+} confirmed
Yellow ppt.		
6. Take the washed yellow ppt. in a test tube and boil it with 2-3 mL of yellow ammonium sulphide.	Yellow ppt. remains insoluble	Cd^{2+} indicated
7. Treat the yellow ppt. with 50% HNO_3 and warm.	Yellow ppt. is soluble and a solution of $Cd(NO_3)_2$ is obtained.	Cd^{2+} indicated
Divide the solution in two parts		
(*i*) To one part of the solution and aqueous ammonia solution followed by excess of ammonia soiution.	A white ppt. of $Cd(OH)_2$ is formed, which dissolves in excess of ammonia.	Cd^{2+} confirmed
Pass H_2S through the solution.	Yellow ppt. of CdS	Cd^{2+} confirmed
(*ii*) To the other part of the solution add $K_4[Fe(CN)_6]$	A bluish white ppt. is formed.	Cd^{2+} confirmed
8. (*i*) Take the washed yellow ppt. and boil it with yellow ammonium sulphide solution given in test 6).	Yellow ppt. dissolves forming soluble ammonium thioarsenate.	As^{3+} indicated
(*ii*) To the solution add dilute HCl	Yellow ppt. of As_2S_3 is obtained	As^{3+} confirmed
9. Dissolve the ppt. obtained in test 8(11) in conc NHO_3. To this	Yellow ppt. of ammonium arsenomolyb-	As^{3+} confirmed

Contd.

solution or to the **O.S.** add **2-3** mL of conc. **HNO$_3$** and ammonium molybdate solution. Boil the mixed solution.	date of obtained.	
Orange ppt.		
10. (*i*) Take the washed orange ppt. in a test tube and boil it with yellow ammonium sulphide (as given in test 6)	Orange ppt. dissolves forming soluble ammonium thioantimonate.	**Sb^{3+} indicated**
(*ii*) Acidify the solution with dilute HCl.	Orange ppt. is obtained.	**Sb^{3+} corfirmed**
11. Boil the ppt. obtained in test 10(11)with 5 mL conc. HCl for 5 min. and pass H$_2$S gas through the hot solution.	Orange ppt. is obtained.	**Sb^{3+} corfirmed**

The chemistry underlying the tests performed (Table 8.12) to identify Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, As^{3+} and Sb^{3+} is outlined below :

Reactions

1. Sulphides of lead and copper dissolve in nitric acid to give a colourless solution of lead nitrate and bluish green solution of copper nitrate. Sulphur is precitated.

$$\underset{\text{(Black)}}{3PbS}+8HNO_3 \longrightarrow \underset{\text{(Colourless)}}{3Pb(NO_3)_2}+3S+2NO+4H_2O$$

$$\underset{\text{(Black)}}{CuS}+8HNO_3 \longrightarrow \underset{\text{(Bluish-green)}}{3Cu(NO_3)_2}+3S+2NO+4H_2O$$

2. Lead nitrate solution reacts with dil. H_2SO_4 forming a white ppt. of lead sulphate

$$Pb(NO_3)_2+H_2SO_4 \longrightarrow \underset{\text{(White)}}{PbSO_4(s)}+2HNO_3$$

which can dissolve in the solution of ammonium acetate.

$$PbSO_4+2NH_4OOCCH_3 \longrightarrow \underset{\text{(Soluble)}}{(CH_3COO)_2Pb}+(NH_4)_2SO_4$$

3. Bluish-green solution of copper nitrate reacts with aqueous ammonia and forms ppt. which dissolves in excess of ammonia solution giving a deep blue solution. Precipitate of $Cu(OH)_2$ dissolves due to the formation of soluble complex.

$$Cu(NO_3)_2+4NH_4OH \longrightarrow \underset{\substack{\text{Tetra-ammine}\\ \text{Copper (II) nitrate}\\ \text{(Deep blue)}}}{[Cu(NH_3)_4](NO_3)_2}+4H_2O$$

4. Copper salt solution reacts with a solution of potassium ferrocyanide giving a chocolate brown ppt.

$$2Cu^{2+}+[Fe(CN)_6]^{4-} \longrightarrow \underset{\substack{\text{Copper hexacyanoferrate (II)}\\ \text{(Chocolate brown)}}}{Cu_2[Fe(CN)_6]}$$

5. Mercuric sulphide being insoluble, on heating with aqua regia goes into solution.

$$3HgS+2HNO_3+6HCl \longrightarrow 3HgCl_2+2NO+3S+4H_2O$$

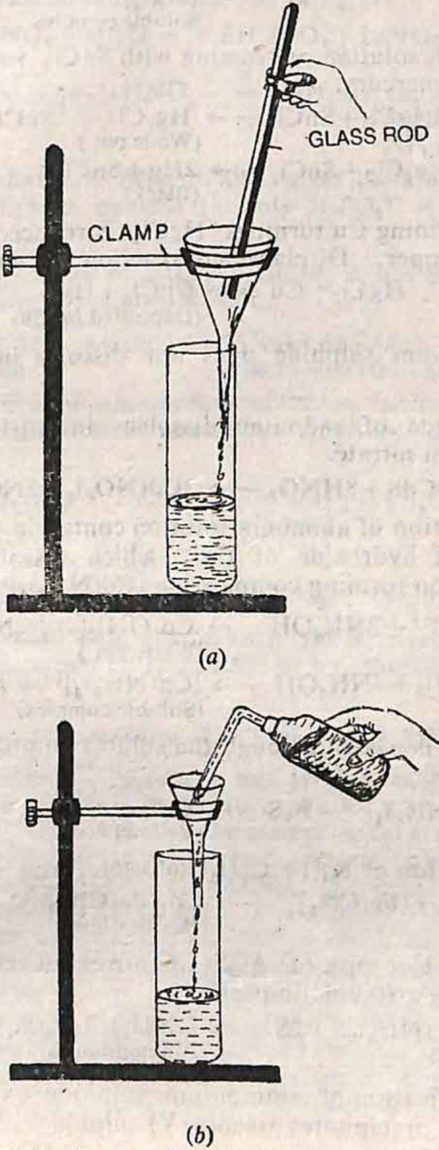


Fig. 8.12. (a) Removing the ppt. from the filter paper by piercing a hole in the filter paper, and (b) washing it down with a liquid from wash bottle.

(*i*) $HgCl_2$ solution on treating with KI solution gives red ppt. which dissolves in excess of KI solution.

$$Hg^{2+} + 2I^- \longrightarrow \underset{\text{(Red)}}{HgI_2(s)}$$

$$HgI_2+2I^- \longrightarrow \underset{\text{Soluble complex}}{[HgI_4]^{2-}}$$

(*ii*) $HgCl_2$ solution on treating with $SnCl_2$ solution gets reduced to metallic mercury.

$$2HgCl_2+SnCl_2 \longrightarrow \underset{\text{(While ppt.)}}{Hg_2Cl_2} + SnCl_4$$

$$Hg_2Cl_2+SnCl_2 \longrightarrow \underset{\text{(Black)}}{2Hg}+SnCl_4$$

(*iii*) On adding Cu turnings $HgCl_2$ is reduced to Hg which is deposited on copper. Displacement reaction takes place.

$$HgCl_2+Cu \longrightarrow CuCl_2+\underset{\text{(Deposited on Cu)}}{Hg}$$

6. Cadmium sulphide does not dissolve in ammonium sulphide.

7. Sulphide of cadmium dissolves in nitric acid forming soluble cadmium nitrate.

$$3CdS+8HNO_3 \longrightarrow 3Cd(NO_3)_2+2NO+3S+4H_2O$$

(*i*) Addition of ammonia solution containing Cd^{2+} ions causes precipitation of hydroxide of Cd^{2+} which dissolves in excess of ammonia solution forming complex ion $[Cd(NH_3)_4]^{2+}$

$$Cd^{2+}+2NH_4OH \longrightarrow \underset{\text{(White ppt.)}}{Cd(OH)_2(s)}+2NH_4^+$$

$$Cd(OH)_2+4NH_4OH \longrightarrow \underset{\text{(Soluble complex)}}{[Cd(NH_3)_4]^{2+}}+4H_2O+2OH^-$$

When H_2S is passed through the soluble complex, a yellow ppt. of CdS is obtained.

$$[Cd(NH_2)_4]^{2+}+H_2S \longrightarrow \underset{\text{(Yellow)}}{CdS(s)}+2NH_4^++2NH_3$$

(*ii*) Addition of $K_4[Fe(CN)_6]$ solution forms bluish white ppt.

$$2Cd^{2+}+[Fe(CN_6]^{4-} \longrightarrow \underset{\text{(Bluish white)}}{Cd_2[Fe(CN)_6](s)}$$

8. (*i*) Yellow ppt. of As_2S_3 dissolves in yellow ammonium sulphide forming a soluble thiosalt.

$$\underset{\text{(Yellow)}}{As_2S_3}+3(NH_4)_2S+2S \longrightarrow \underset{\text{Ammonium thioarsenate}}{2(NH_4)_3AsS_4(aq)}$$

(*ii*) Acidification of ammonium sulphide extract containing thiosalts of As^{3+} precipitates arsenic (V) sulphide. Some sulphur is also precipitated.

$$2(NH_4)_3AsS_4+6HCl \longrightarrow 6NH_4Cl+3H_2S+\underset{\text{(Yellow)}}{As_2S_5(s)}$$

9. Nitric acid reacts with As_2S_5 and forms soluble H_3AsO_4 (arsenic acid). Arsenic salt on reacting with conc. nitric acid is oxidized to arsenic acid.

Arsenic acid solution reacts with ammonium molybdate forming a yellow ppt. of arsenomobyldate.

$$3As_2S_5+10HNO_3+4H_2O \longrightarrow \underset{\text{Arsenic acid}}{6H_3AsO_4}+10NO+15S$$

$$H_3AsO_4+12(NH_4)_2MoO_4+21HNO_3 \longrightarrow \underset{\text{(Yellow)}}{(NH_4)_3[AsMo_{12}O_{40}](s)} +21NH_4NO_3+12H_2O$$

Note. Phosphate, if present, also gives a similar test (tests). As^{3+} should be confirmed by this test only if PO_4^{3-} is absent in the salt/mixture.

10. (*i*) Orange ppt. of Sb_2S_3 dissolves in hot yellow ammonium sulphide forming a soluble thiosalt.

$$\underset{\text{(Orange)}}{Sb_2S_3}+3NH_4S+2S \longrightarrow \underset{\text{(Ammonium thioantimonate)}}{2(NH_4)_3SbS_4(aq)}$$

(*ii*) Acidification of ammonium sulphide extract containing thiosalt of Sb^{3+} precipitates antimony (V) sulphide Some sulphur is also precipitated.

$$2(NH_4)_3SbS_4+6HCl \longrightarrow \underset{\text{(Orange)}}{Sb_2S_5(s)}+6NH_4Cl+3H_2S$$

11. Sb_2S_5 dissolves in conc. HCl

$$Sb_2S_5+6HCl \longrightarrow 2SbCl_3(aq)+2S+3H_2S$$

Now on passing H_2S gas through the solution, antimony is precipitated as Sb_2S_3 which is identified by its characteristic orange colour.

Analysis of Group III Cations (Fe^{2+}, Fe^{3+} and Al^{3+})

After the analysis of groups I and II proceed for identifying the cations of group III. To do this take 2.3 mL of O.S. if both groups I and II have been found to be absent or take the solution of group II (when group II is absent) and filtrate (when group II is present) boil for sufficient time to remove H_2S completely and also concentrate the solution to 5 mL. Add about 0.5 mL of conc. HNO_3* and boil to oxidize Fe^{2+} to Fe^{3+}. Oxidation is necessary otherwise precipitation of iron will be incomplete Now to this add 0.5 g of solid NH_4Cl, followed by aqueous ammonia solution until the solution distinctly smells of ammonia. The formation of a precipitate indicates the presence of group III. Filter the precipitate and analyse the ppt. of the group III as given in the Table 8.13. Store the filtrate.

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*The presence of Fe^{2+} or Fe^{3+} ions can be tested before adding nitric acid. For this take 1 mL of original solution and add a few drops of potassium ferricyanide. Appearance of a deep blue colour or ppt. shows the presence of Fe^{2+}. Similarly take 1 mL of the group solution and add a few drops of potossium ferrocyanide. Appearance of a deep blue colonr confirms the presence of Fe^{3+}.

$$3Fe^{2+}+NO_3^-+4H^+ \longrightarrow 3Fe^{3+}+NO+2H_2O$$

$$Fe^{3+}+3OH^- \longrightarrow \underset{\text{(Brown)}}{Fe(OH)_3(s)}$$

$$Al^{3+}+3OH^- \longrightarrow \underset{\text{(White gelatinous)}}{Al(OH)_3(s)}$$

Note. Ammonium chloride controls the ionization of ammonium hydroxide (common ion effect). In the absence of ammonium chloride, cations of subsequent groups such as Zn^{2+} and Mn^{2+} may also be precipitated along with the hydroxides of Fe^{3+} and Al^{3+}. Ammonium chloride reduces the concentration of OH^- by common ion effect and buffer action and thus prevents the metals of subsequent groups from being precipitated as hydroxides, which have higher solubility product values than those of the hydroxides of group III cations.

Table 8.13. Analysis of group III cations (Fe^{2+}, Fe^{3+} and Al^{3+})

Experiment	*Observation*	*Inference*
1. Treat the brown ppt. of $Fe(OH)_3$ with dilute HCl and heat. Divide the solution into two parts :	A yellow solution is obtained due to the formation of $FeCl_3$	Fe^{3+} indicated
(*i*) To one part add potassium ferrocyanide solution.	Deep blue colour or ppt. is obtained	Fe^{3+} confirmed
(*ii*) To the 2nd part of the solution add potassium sulphocyanide solution.	A deep red coloration results	Fe^{3+} confirmed
2. (*i*) To the O.S. add a few drops of dilute HCl followed by potassium ferricyanide solution.	Deep blue colour or ppt. is obtained	Fe^{2+} present
(*ii*) To the O.S. add a few drops of HCl followed by potassium thiocyanate solution.	No coloration results	Fe^{2+} present
3. Dissolve the white gelatinous ppt. in a minimum quantity of dil. HCl. Now add a few drops of blue litmus solution followed by ammonia solution until the solution becomes ammonical.	A blue floating ppt. in colourless solution (lake)	Al^{3+} confirmed

The chemistry underlying the tests (Table 8.13) performed to identify Fe^{2+}, F^{3+} and Al^{3+} ions is outlined below :

Reactions

1. The brown ppt. of $Fe(OH)_3$ dissolves in hot dilute HCl forming a yellow solution of ferric choride.

$$Fe(OH)_3+3HCl \longrightarrow \underset{\text{(Yellow)}}{FeCl_3(aq)}+3H_2O$$

(*i*) Solution containing ferric (III) ions reacts with potassium ferrocyanide, $K_4[Fe(CN)_6]$ to give deep blue ppt. (Prussian blue).

$$Fe^{3+} + K_4[Fe(CN)_6] \longrightarrow \underset{\substack{\textbf{(Prussian blue)}\\ \textbf{Potassium ferri-ferrocyanide}}}{KFe[Fe(CN)_6](s)} + 3K^+$$

(*ii*) Solution containing Fe (III) ions reacts with potassium thiocynate solution to give a deep red coloration caused by ferrithiocyanate ion, $[Fe(SCN)]^{2+}$.

$$Fe^{3-} + SCN^- \longrightarrow \underset{\textbf{(Deep red)}}{[Fe(SCN)]^{2+}(aq)}$$

2. (*i*) Solution containing Fe^{2+} ions reacts with potassium ferricyanide to give deep blue ppt. (Turnbull's blue)

$$Fe^{3+} + K_3[Fe(CN)_6] \longrightarrow \underset{\substack{\textbf{(Turnbull's blue)}\\ \textbf{Potassium ferro-ferricyanide}}}{KFe[Fe(CN)_6]} + 2K^+$$

(*ii*) Ferrous ions do not give any coloration with potassium thiocyanate solution.

3. A white gelatinous ppt. of $Al(OH)_3$ is obtained in the reaction solution which absorbs the blue colouring matter of litmus and turns blue.

$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

$$AlCl_3 + 3NH_4OH \longrightarrow 3NH_4Cl + Al(OH)_3(s)$$

The ppt. of $Al(OH)_3$ absorbs blue colouring matter of litmus and floats in the body of the solution (lake test).

Analysis of Group IV Cations (Ni^{2+}, Zn^{2+}, Mn^{2+} and Co^{2+})

In case the cations from group I, II and III are absent, take 2-3 mL of the original solution and add to it 0.5 g NH_4Cl and aqueous ammonia dropwise until it smells like ammonia, and if cations from group I, II and III are present take the filtrate of group III, smell it and make it ammonical if necessary. Now pass H_2S gas through a test portion. If a ppt. is formed, it shows the presence of group IV. Now pass H_2S through the whole solution for sufficient time to ensure complete precipitation. If a precipitate (black, dirty white, or buff coloured) appears, group IV is present. Filter and separate the ppt. and store the filtrate. Analyse the ppt. for group IV cations as given in the Table 8.14.

$$Zn^{2+} + H_2S \longrightarrow \underset{\textbf{(White)}}{ZnS(s)} + 2H^+$$

$$Ni^{2+} + H_2S \longrightarrow \underset{\textbf{(Black)}}{NiS(s)} + 2H^+$$

$$Mn^{2+} + H_2S \longrightarrow \underset{\textbf{(Buff)}}{MnS(s)} + 2H^+$$

$$Co^{2+} + H_2S \longrightarrow \underset{\textbf{(Black)}}{CoS(s)} + 2H^+$$

Table 8.14. Analysis of group IV cations (Ni^{2+}, Zn^{2+}, Mn^{2+} and Co^{2+})

Experiment	*Observation*	*Inference*
Black ppt.		
1. Dissolve the black ppt. by heating with a minimum volume of aqua-regia (3 parts HCl and 1 part HNO_3). Evaporate nearly to dryness. Cool and dissolve in water. Divide the solution in three parts.	Residue is obtained due to the formation of anhydrous chlorides of Ni^{2+} or Co^{2+}	Ni^{2+} or Co^{2+} present
(*i*) To one part of the solution (or O.S.) add a few drops of dimethylglyoxime followed by aqueous ammonia solution.	A bright red ppt. of bis (dimethylglyoximato) nickel (II) is obtained	Ni^{2+} confirmed
(*ii*) To the 2nd part of the solution (or O.S.) add acetic acid and a little KNO_2. Allow it to stand with occasional scratching and shaking.	A yellow ppt. of potassium cobaltinitrite is obtained.	Co^{2+} present
(*iii*) To the 3rd part of the solution (or O.S.) add 1 g of ammonium thiocyanate, 2 mL of amyl alcohol (or 2 mL acetone). Shake the contents well.	Blue colour in the organic solvent layer	Co^{2+} confirmed
(*iv*) Both Co^{2+} and Ni^{2+} can also be confirmed by borax-bead test.		
Dirty white ppt.		
2. Treat the dirty white ppt. with a small volume of dil. HCl. Boil the contents to remove H_2S. Cool the solution. Divide the solution in two fractions.		
(*i*) To one fraction of the solution add NaOH solution slowly.	A white ppt. appears which dissolves in excess of NaOH	Zn^{2+} present
(*ii*) To the 2nd fraction of the solution add 1 mL of $K_4[Fe(CN)_6]$ solution.	A bluish white ppt. appears	Zn^{2+} confirmed
3. Perform charcoal cavity cobalt nitrate test with the original salt or with the white ppt.	A green mass confirms Zn^{2+}	Zn^{2+} confirmed
Buff coloured ppt.		
4. (*i*) Take a part of the buff coloured ppt. and add dil. HCl. Boil the contents to boil off H_2S gas. Cool the solution and add NaOH	A white ppt. $[Mn(OH)_2]$ is formed which turns brown due to atmospheric oxidation	Mn^{2+} present

Contd.

solution slowly. Warm a little.		
(*ii*) Dissolve the other part of the ppt. (or the salt itself) in conc. HNO_3. Add 1 g of lead peroxide and boil the contents. Allow it to stand.	The solution acquires pink colour due to the formation of permanganic acid	Mn^{2+} confirmed
(*iii*) Perform borax bead test with a little of the residue and note the colour of the bead.	Violet bead in oxidizing flame	Mn^{2+} confirmed

The chemistry underlying the tests (Table 8.14) performed to identify Ni^{2+}, Co^{2+}, Zn^{2+} and Mn^{2+} ions is outlined below :

Reactions

1. Black ppt. of nickel sulphide and cobalt sulphide dissolves in aqua regia.

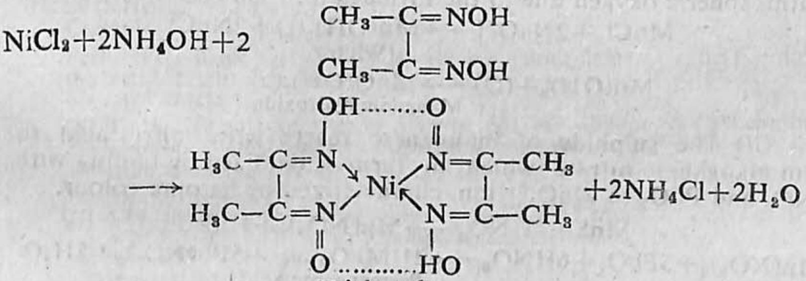
$$3NiS + 2HNO_3 + 6HCl \longrightarrow 3NiCl_2 + 2NO + 2S + 4H_2O$$

$$3CoS + 2HNO_3 + 6HCl \longrightarrow 3CoCl_2 + 2NO + 3S + 4H_2O$$

Hydrated chlorides on evaporation to dryness, yield residue of anydrous chlorides.

$$\underset{\text{(Green)}}{NiCl_2.6H_2O} \xrightarrow[\text{dryness}]{\text{Heat to}} \underset{\text{(Yellow)}}{NiCl_2} + 6H_2O$$

(*i*) A nickel salt solution reacts with dimethylglyoxime (DMG) solution in the presence of ammonia solution forming a bright red ppt. of bis (dimethylglyoximato) nickel (II) complex.



$$NiCl_2 + 2NH_4OH + 2\,\begin{array}{l}CH_3-C=NOH\\ \quad\;\;|\\ CH_3-C=NOH\end{array} \longrightarrow [\text{complex}] + 2NH_4Cl + 2H_2O$$

(Bright red)

(*ii*) Cobalt salt solution reacts with KNO_2 solution in the presence of acetic acid forming a yellow crystalline ppt. of potassium cobaltinitrite.

$$Co^{2+} + 7NO_2^- + 3K^+ + 2H^+ \longrightarrow K_3[Co(NO_2)_6] + NO + H_2O$$

(*iii*) With ammonium thiocyanate solution, cobalt ions form a blue coloured complex, ammonium cobalt thiocyanate, $NH_4[Co(CNS)_4]$.

This is a stable complex and gets extracted into organic solvent.

$$Co^{2+} + 4NH_4CNS \longrightarrow \underset{\text{(Blue)}}{(NH_4)_2[Co(CNS)_4]} + 2NH_4^+$$

2. White ppt. of zinc sulphide is soluble in dil. HCl. A colourless solution of zinc chloride is obtained and hydrogen sulphide escapes.

$$ZnS + 2HCl \longrightarrow ZnCl_2(aq) + H_2S(g)$$

(*i*) Solution containing Zn^{2+} ions on treating with sodium hydroxide solution gives a white ppt. of zinc hydroxide which dissolves in excess of alkali, forming soluble sodium zincate.

$$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2(s) + NaCl$$

$$Zn(OH)_2 + 2NaOH \longrightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2(aq)} + 2H_2O$$

(*ii*) Solution containing Zn^{2+} reacts with potassium ferrocyanide solution and produces a bluish white ppt. of zinc hexacynoferrate (II).

$$2ZnCl_2 + K_4[Fe(CN)_6] \longrightarrow 4KCl + \underset{\text{Zinc hexacynoferate (II)}}{Zn_2[Fe(CN)_6]}$$

3. It has already been explained under the charcoal cavity test.

4. (*i*) Buff coloured ppt. of MnS is soluble in dil. HCl.

$$MnS + 2HCl \longrightarrow MnCl_2 + H_2S$$

Solution when treated with sodium hydroxide solution gives a whith ppt. of manganese hydroxide which turns brown on exposure to atmospheric oxygen due to the formation of manganic hydroxide.

$$MnCl_2 + 2NaOH \longrightarrow \underset{\text{(White)}}{Mn(OH)_2(s)} + 2NaCl$$

$$Mn(OH)_2 + (O) \longrightarrow \underset{\text{Manganic hydroxide}}{MnO(OH)_2(s)}$$

(*ii*) The sulphide of manganese reacts with nitric acid to form manganese nitrate which in turn is oxidized by boiling with HNO_3 and PbO_2 to MnO_4^{2-} ion, characterized by its pink colour.

$$MnS + 2HNO_3 \longrightarrow Mn(NO_3)_2 + H_2S$$

$$2Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 \longrightarrow \underset{\substack{\text{Permanganic acid} \\ \text{(Pink)}}}{2HMnO_4(aq)} + 5Pb(NO_3)_2 + 2H_2O$$

(*iii*) The chemistry of borax bead test has already been explained in the beginning of this unit.

Analysis of Group V Cations (Ca^{2+}, Sr^{2+} **and** Ba^{2+})

When the first four groups are absent, take the original solution other wise take the filtrate of the fourth group. Add conc. $(NH_4)_2CO_3$ solution with constant stirring to the above solution.

Warm and allow to stand. Formation of a white ppt. indicates the presence of group V. Filter the ppt. Analyse the ppt. for the group V cations as given in the Tables 8.15 and store the filtrate.

$$Ca^{2+}+CO_3^{2-}\longrightarrow CaCO_3(s)$$
$$Ba^{2+}+CO_3^{2-}\longrightarrow BaCO_3(s)$$
$$Sr^{2+}+CO_3^{2-}\longrightarrow SrCO_3(s)$$

Table 8.15. Analysis of group V cations (Ba^{2+}, Sr^{2+} and Ca^{2+})

The white ppt. may contain $BaCO_3$, $SrCO_3$ and $CaCO_3$. Wash the ppt. with hot water and reject washings. Dissolve the ppt. in minimum amount of hot dil. CH_3COOH. Divide the solution in four parts.

$$BaCO_3+2CH_3COOH\longrightarrow Ba(CH_3COO)_2+H_2O+CO_2$$
$$CaCO_3+2CH_3COOH\longrightarrow Ca(CH_3COO)_2+H_2O+CO_2$$
$$SrCO_3+2CH_3COOH\longrightarrow Sr(CH_3COO)_2+H_2O+CO_2$$

Experiment	*Observation*	*Inference*
1. To one part of the solution add potassium chromate solution.	A yellow ppt. of barium chromate is obtained.	Ba^{2+} confirmed
2. To the 2nd part of the solution add dil. H_2SO_4 solution.	A white ppt. of $BaSO_4$ is obtained. The ppt. is insoluble in all mineral acids.	Ba^{2+} confirmed
3. Perform flame test with the salt or with the ppt. obtained in test 1. (Group ppt. *i.e.*, carbonate can also be used for the flame test).	A light green flame.	Ba^{2+} confirmed
4. To the 3rd part of the solution and conc. solution of $(NH_4)_2SO_4$ and warm if necessary.	A white ppt. of $SrSO_4$ is obtained.	Sr^{2+} confirmed
5. Perform the flame test with the salt or with the ppt. obtained in test 1.	A crimson colour flame.	Sr^{2+} confirmed
6. (*i*) To the 4th part of the solution add conc. ammonium oxalate solution and heat.	A white ppt. of calcium oxalate is obtained.	Ca^{2+} confirmed
(*ii*) Add to the ppt. obtained, dil. H_2SO_4. Now add a few drops of dilute $KMnO_4$ solution.	Pink colour of KMnO solution is discharged.	Ca^{2+} confirmed
7. Perform flame test with the salt or with the ppt. obtained in test 6.	A brick red flame is seen.	Ca^{2+} confirmed

The chemistry underlying the tests (Table 8.15) performed for identfying the group V cations is outlined on next page :

Reactions

1. Solution of barium acetate reacts with potassium chromate to form a yellow ppt. of barium chromate.

$$(CH_3COO)_2Ba+K_2CrO_4 \longrightarrow \underset{\text{(Yellow)}}{BaCrO_4(s)}+2CH_3COOK$$

2. Solution of barium acetate reacts with dilute H_2SO_4 to yield a white crystalline ppt. of barium sulphate which is insoluble in all acids.

$$(CH_3COO)_2Ba+H_2SO_4 \longrightarrow \underset{\text{(White)}}{BaSO_4(s)}+2CH_3COOH$$

3. The principle of flame test has already been explained.

4. Solution of strontium acetate reacts with ammonium sulphate solution forming a white ppt. of strontium sulphate which is insoluble in mineral acids.

$$(CH_3COO)_2Sr+(NH_4)_2SO_4 \longrightarrow \underset{\text{(White)}}{SrSO_4(s)}+2CH_3COONH_4$$

5. The principle of the flame test has already been explained.

6. (*i*) Solution of calcium acetate reacts with ammonium oxalate to yield a white ppt. of calcium oxalate.

$$(CH_3COO)_2Ca+(NH_4)_2C_2O_4 \longrightarrow \underset{\text{(White)}}{CaC_2O_4(s)}+2CH_3COONH_4$$

(*ii*) The ppt. of calcium oxalate is soluble in dil. HCl or H_2SO_4 and forms the corresponding salt solution.

$$CaC_2O_4+2HCl \longrightarrow CaCl_2+H_2C_2O_4 \text{ [or } (COOH)_2]$$

The solution acts as a reducing agent due to the presence of oxalate ions and discharges the colour of $KMnO_4$ solution.

Analysis of Group VI Cations (Mg^{2+}, and K^+)

This group includes those elements which are not precipitated by other group precipitating reagents. There is, however, no group test for these cations and the different cations are tested individually as given in Table 8·16.

Concentrate the filtrate obtained from Group V by evaporation. Now add $(NH_4)_2SO_4$ and $(NH_4)C_2O_4$ solutions and boil the solution to ensure the complete removal of Group V cations. If a ppt. appears, filter and reject the ppt. The clear solution thus obtained is evaporated to dryness and heated until all the ammonium salts have been decomposed or volatilized. A residue left in the evaporating dish dissolved in 5 mL water. If it does not dissolve completely add a few drops of dilute HCl. Divide the solution in parts and procced as given in Table 8.16.

Table 8.16. Analysis of group VI cations (Mg^{2+} and K^+)

Experiment	*Observation*	*Inference*
1. To one part of the solution add solid NH_4Cl followed by disodium hydrogen phosphate solution (or ammonium phosphate). Mix the contents thoroughly. Add a few mL of aqueous solution of ammonia until it smells of ammonia. Add a few mL of ethanol and scratch the sides of the test tube with a glass rod.	A fine crystaline white ppt. appears on scratching the sides of the test tube.	Mg^{2+} confirmed
2. To the other part of the solution add a few drops magneson I reagent (a alkaline solution of p-nitrobenzene azo-resorcinol) and NaOH solution to make it alkaline.	A blue colour or ppt. appears.	Mg^{2+} confirmed
3. To another part of solution add a few drops of titan yellow solution. Add a few mL of NaOH solution to make if alkaline.	A red ppt. appears.	Mg^{2+} confirmed

Note : If Mg^{2+} is absent then proceed as suggated below for the detection of K^+.

Experiment	*Observation*	*Inference*
4. To another part of the solution (HCl free) add a few drops of acetic acid and freshly prepared solution of sodium cobaltinitrite. Shake and allow it to stand.	Abright yellow ppt. of $K_4Na[Co(NO)_6]$ is obtained.	K^+ present
5. Perform the flame test with another part of the solution.	A violet flame but intense violet red (or crimson) through blue glass.	K^+ confirmed

Note : While performing the tests of K^+, ammonium salts should be absent as they tend to interfere in its detection.

The chemistry involved in the tests (Table 8.16) performed for identifying Mg^{2+} and K^+ ions is given below.

Reactions

1. A magnesium salt solution reacts with a phosphate in the presence of ammonia to form a fine crystalline white ppt. of magnesium ammonium phosphate hexahydrate.

$$Mg^{2+} + HPO_4^{2-} + NH_4OH + 5H_2O \longrightarrow \underset{\text{(White ppt.)}}{MgNH_4PO_4.6H_2O}$$

Ethanol decreases the solubility of ppt.

2. Magnesium salt solution in the presence of NaOH solution forms a blue colour solution or ppt. with magneson I reagent.

$$Mg^{2+} + 2OH^- + \text{Magnesium} \longrightarrow \underset{\text{(Blue colour or ppt.)}}{Mg(OH)_2 \ \text{Magnesium}}$$

3. Alkaline magnesium salt solution forms a red coloured ppt. with titan yellow solution.

4. Addition of sodium cobaltinitrite to a solution containing K^+ ions gives a yellow crystalline ppt. of potassium sodiocobaltinitrite.

$$2KCl + Na_3[Co(NO_2)_6] \longrightarrow K_2Na[Co(NO_2)_6] + 2NaCl$$

The precipitation reaction is also shown by NH_4^+ ions. Hence, the test for K^+ ion should be performed in the absence of NH_4^+ ion. If NH_4^+ ions are present they should be removed from the solution by boiling it with Na_2CO_3 or NaOH before performing the test.

5. The chemistry of the flame test has already been discussed in the beginning of this unit.

SPECIMEN RECORD OF MIXTURE ANALYSIS

Experiment : To analyse the given mixture containing two cations and two anions.

Experiment	*Observation*	*Inference*
Dry Tests		
1. Observe the colour of the mixture	Bluish-green colour	Cu^{2+}, Ni^{2+} may be present
2. Heat a small amount mixture in a dry test tube	White fumes with pungent smell, which give dense white fumes with aqueous solution of ammonia	May be Cl^- present
3. Perform the flame test with a small amount of mixture	Bluish green flame	Cu^{2+} may be present
4. Perform the borax bead test with the mixture	Green bead when hot, blue when cold	Cu^{2+} may be present
5. Heat a small part of the mixture/fusion mixture in charcoal cavity in the reducing flame	Red scales	Cu^{2+} may be present
6. Treat a small amount of the mixture with dilute H_2SO_4. If necessary heat.	No apparent action, No smell of any kind.	CO_3^{2-}, S^{2-}, SO_3^{2-}, NO_2^-, *etc.* absent
7. Treat the mixture with conc. H_2SO_4.	Colourless gas with pungent odour (HCl), which forms dense white fumes (NH_4Cl) with aqueous ammonia solution	Cl^- may be present

Coutd.

Experiment	*Observation*	*Inference*
Wet Tests (Acid Radicals)		
8. Prepare the clear and transparent sodium carbonate extract (S.E.) of the mixture		
9. To 1 mL of S E., add dil. HNO_3 to acidify it. Add $AgNO_3$ solution	White ppt. soluble in aqueous NH_3 solution	Cl^- confirmed
10. To ~1 g mixture add solid K_2CrO_7+conc. H_2SO_4, heat the contents, pass the red vapours through NaOH solution (chromyl-chloride test)	Yellow solution of sodium chromate is obtained	Cl^- confirmed
Acidify the yellow solution with acetic acid and add lead acetate solution	Yellow ppt. of lead chromate obtained.	
11. To another portion of S.E. add dilute HCl and $BaCl_2$ solution	White ppt. of $BaSO_4$ insoluble in any mineral acid	SO_4^{2-} confirmed
Wet Tests (Basic Radicals)		
12. Treat the mixture with NaOH solution and heat	No NH_3 gas evolved	NH_4^+ absent
13. Prepare the clear and transparent solution in water or dil. or conc. HCl		
14. To O.S. add dil. HCl and heat and cool	No white ppt.	Group I absent
15. Pass H_2S gas through the above solution and filter	Black ppt.	Group II present
16. Filter and wash the black ppt. and dissolve in 3-4 mL 50% HNO_3	ppt. dissolves	Hg^{2+} absent
17. To one part of the above solution add dil H_2SO_4 and a few drops of ethyl alcohol	No white ppt.	Pb^{2+} absent
18. To the remaining part of solution add aqueous NH_3 solution in excess	Deep blue colouration	Cu^{2+} may be present
19. To the above deep blue solution, add CH_3COOH and $K_4[Fe(CN)_6]$ solution	Chocolate coloured ppt. of $Cu_2[Fe(CN)_6]$ appeares	Cu^{2+} confirmed
20. Boil off the H_2S gas from the filtrate obtained from group II and boil the solution with 1 mL of HNO_3 and cool. Add solid NH_4Cl and aqueous ammonia solution in cxcess	White gelatinous ppt.	Al^{3+} may be present
21. Filter the white ppt. and dissolve the ppt. in dil. HCl		
To the above solution add blue litmus solution, followed by the drop by drop addition of aqueous ammonia solution until the solution is just alkaline	A blue-red lake	Al^{3+} confirmed

Result : The given mixture contains : anions Cl^-, SO_4^{2-}
cations Cu^{2+}, Al^{3+}.

ORAL QUESTIONS AND ANSWERS

Q. 8.1. What is quatitative inorganic analysis ?

Ans. The detection of acidic and basic radicals present in a given salt/mixture is called qualitative inorganic analysis.

Q. 8.2. What are preliminary tests ?

Ans. These are the tests which indicate the presence of acidic or basic radicals in the salt/mixture. These are performed before starting the systematic analysis.

Q. 8.3. What is a reagent ?

Ans. The solution employed for carrying out a test is called a reagent.

Q. 8.4. What is a group reagent ?

Ans. The reagent which is employed in identifying a group of radicals is known as a group reagent.

Q. 8.5. Why do salts of the following ions Cu^{2+}, Ba^{2+}, Sr^{2+}, Ca^{2+}, Na^{2+} and K^+ impart colour to the flame ?

Ans. This is due to the fact that the chlorides of these cations are volatile and at higher temperature they ionize giving respective cations. These cations then impart colour to the flame.

Q. 8.6. Why is HCl employed in flame test ?

Ans. Only the volatile compounds of cations impart colour to the flame. Only metal chlorides are volatile whereas their sulphates, nitrates, *etc.* are not. Thus, HCl is used to convert cations into their volatile chlorides.

Q. 8.7. What is the principle of flame test ?

Ans See Section 8.3.3.

Q. 8.8. What type of flame is employed to perform the flame test ? How is it obtained ?

Ans. A non-luminuous flame is employed to perform the test. It is obtained by keeping the holes of the burner open.

Q. 8.9. Why is a green flame not obtained in the case of barium sulphate or phosphate ?

Ans. Both barium sulphate and phosphate are insoluble and cannot be easily converted into chlorides. Therefore, the green flame is either indistinct or visible with difficulty.

Q. 8.10. Why is platinum wire used for flame test ?

Ans. This is because the metals other than platinum are attacked by conc. HCl, while platinum wire does not react with conc. HCl even at very high temperature.

Q. 8.11. Can we perform the charcoal cavity test without the addition of fusion mixture (Na_2CO_3 and K_2CO_3) with the carbonate of metals ?

Ans. Yes, we can directly perform the charcoal cavity test without the addition of fusion mixture because the latter simply converts the substances into carbonates in fused state. Carbonates of metals on heating in charcoal cavity are reduced to metallic state.

Q. 8.12. Why do we not perform borax bead test with the white salts ?

Ans. This test is applied for the identification of the cations of the coloured salt only because the borax forms the corresponding metaborates which possess characteristic colour. For example, with $CuSO_4$, the reaction is

$$\underset{}{CuSO_4}+\underset{\text{(From borax)}}{B_2O_3} \longrightarrow \underset{\text{(Blue)}}{Cu(BO_2)_2}+SO_3$$

Q. 8.13. What is the composition of the bead obtained when borax is heated in the flame ?

Ans. It consists of a mixture of sodium metaborate and boric anhydride.

Q. 8.14. Why is a small quantity of mixture used in the borax bead test ?

Ans. To avoid the formation dark and opaque bead which in subsequent treatment cannot be recognized easily.

Q. 8.15. Name the cations which can be identified by flame test.

Ans. Cu^{2+}—Bright green
Ca^{2+}—Brick red
Ba^{2+}—Apple green
Sr^{2+}—Crimson
K^{2+}—Lilac

Q. 8.16. What is sodium carbonate extract ? State its uses in qualitative analysis.

Ans. When a salt is insoluble in water, it is the normal practice to convert it into a soluble sodium salt. To get this the mixture is mixed with five times amount of Na_2CO_3 and suspended in water. On boiling for ½ hr or more, sodium salt is produced by double decomposition. The filtrate is used for the detection of anions and is called sodium carbonate extract.

Q. 8.17. Can we use sodium bicarbonate in place of sodium carbonate in preparing the extract for detection of anions ?

Ans. No. Metal bicarbonates formed by double decomposition will remain in solution.

Q. 8.18. Why is sodium carbonate extract acidified before performing the confirmatory tests for anions ?

Ans. Sodium carbonate extract in addition to the sodium salts of anions contain carbonate also. On heating with the test reagent carbonate of certain metal precipitate which interferes in the detection of acid radicals. Because of this, Na_2CO_3 is decomosed by adding HCl, HNO_3, H_2SO_4, depending upon the nature of test.

Q 8.19. Can sodium carbonate extract be used to te t for CO_3^{2-} ions ?

Ans. No, because it already contains these ions.

Q. 8.20. Which gas is evolved by the action of dilute acids on metal carbonates ?

Ans. Carbon dioxide.

Q. 8 21 What is lime water ?

Ans. It is a water solution of calcium hydroxide.

Q. 8.22. Why does lime water turn milky on bubbling CO_2 gas through it ?

Ans. Due to the formation of insoluble $CaCO_3$.

Q. 8.23. Why does the milkiness obtained in the detection of CO_3^{2-} ions by lime water test disappear after some time ?

Ans. Initially $CaCO_3$ (causing milkness) is formed which disappears due to the formation $Ca(HCO_3)_2$ when CO_2 is passed for long.

Q. 8.24 Name the anion which give brown fumes on reacting with dilute/conc. H_2SO_4.

Ans With dilute H_2SO_4 NO_2^- ion gives brown fumes. With conc. H_2SO_4 both Br^- and NO_3^- ions give brown fumes.

Q. 8.25. Name the rotten egg smelling gas. Which ion on reacting with acid gives this gas ?

Ans. H_2S. This gas is evolved where S^{2-} is reacting with dilute H_2SO_4.

Q. 8.26. Why does a paper soaked in $K_2Cr_2O_7$ solution turn green in the detection of SO_3^{2-} ion ?

Ans. The paper turns green because the SO_2 gas evolved from SO_3^{2-} salt reduces $K_2Cr_2O_7$ to $Cr_2(SO_4)_3$ which turns the paper green.

Q. 8 27. Can alter paper dipped in silver nitrate solution instead of lead acetate paper be used for testing a sulphide ?

Ans. Yes, a paper dipped in $AgNO_3$ when exposed to the vapours of H_2S turns black due to the formation of silver sulphide.

$$2AgNO_2+H_2S \rightarrow Ag_2S+2HNO_3$$

Q. 8.28. A gas evolved with effervescence on treating a salt with dil. HCl may be CO_2 or SO_2. How will you distinguish between them ?

Ans. (*a*) SO_2 has a pungent burning sulphur smell whereas CO_2 is odourless.

(*b*) SO_2 turns potassium dichromate paper green, whereas CO_2 does not.

Q. 8.29. How will you distinguish between carbonate and bicarbonate ions ?

Ans. $MgSO_4$ gives a white ppt. with carbonate ions in cold solution while a white ppt. is obtained with bicarbonate ions in hot solution only.

Phenolphthalein gives a pink colour with carbonate ions and no colour is obtained with bicarbonate ions.

Q. 8.30. How can sulphide ions be distinguished form sulphite ions ?

Ans. $AgNO_3$ forms white ppt. with sulphite ions while a black precipitate is obtained with sulphide ions.

$BaCl_2$ gives white ppt. with sulphite ions while no ppt. is obtained with sulphide ions.

$FeCl_3$ solution gives a red colouration with sulphite ions and a black ppt. is formed with sulphide ions.

Q. 8.31. How will you distinguish between sulphate and thiosulphate ions ?

Ans. $AgNO_3$ gives white ppt. with thiosulphate ions which turns black on standing whereas no ppt. is obtained with sulphate ions.

$FeCl_3$ gives purple colour with thiosulphate ions which disappears gradually and no ppt. or colouration is obtained in case of sulphate

Q. 8.32. How will you distinguish between sulphite and sulphate ions ?

Ans. $BaCl_2$ gives a white ppt. with both sulphite and sulphate ions.

$BaSO_3$ is soluble in conc. HCl whereas $BaSO_4$ is insoluble in conc. HCl.

$FeCl_3$ solution gives a red colour with sulphite ion and no colour is obtained with sulphate.

Q. 8.33. How can nitrite ion be distinguished from nitrate ion ?

Ans. Nitrate ion gives a brown ring with $FeSO_4$ and conc. sulphuric acid. But with nitrite ion a black coloured solution is obtained.

Q. 8.34. What is the formula of compound present in brown ring ?

Ans. $3Fe^{2+}+NO_3^-+4H^+ \longrightarrow 3Fe^{3+}+NO+2H_2O$

$FeSO_4+NO \longrightarrow FeSO_4.NO$ or $[Fe(H_2O)_5NO]SO_4$

Q. 8.35. Why is a freshly prepared solution of $FeSO_4$ used for the detection of nitrate and nitrite ions ?

Ans. This is because Fe^{2+} ions on long standing are oxidized to Fe^{3+} ions which are not used for the detection of nitrate or nitrite ions.

Q. 8.36. Why are hydrogen peroxide and silver nitrate kept in coloured bottles ?

Ans. Hydrogen peroxide and silver nitrate are decomposed by sunlight and to avoid their decomposition coloured bottles are used for their storage.

Q. 8.37. Why does only the organic layer assume colour and not the aqueous layer when the tests for halides are done ?

Ans. Both Br_2 and I_2 are covalent. They have preference for organic layer.

Q. 8.38. What happens when chloride, bromide and iodide salts are separately heated with conc. H_2SO_4 ?

Ans. (*a*) Chloride gives HCl gas which gives thick white fumes with aqueous ammonia. (*b*) Bromide gives reddish-brown Br_2 vapours. (*c* Iodide gives violet vapours of iodine which turns starch paper blue.

Q. 8.39. How do you distinguish between Br^- and NO_3^- ions ?

Ans. Treat the salt with conc. H_2SO_4. Pass the reddish-brown gas evolved through $FeSO_4$ solution. If it turns black, it is NO_3^-. In case it does not turn black, the anion is Br^-.

Q. 8.40 Given salt is a bromide or iodide. How will you identify it by treating the salt with chlorine water and CS_2 ?

Ans. If CS_2 layer assumes an orange colour, it is Br^-. If CS_2 layer assumes a violet colour, it is I^-.

Q. 8.41. Why does the chromyl chloride test fail with Br^- and I^- ?

Ans. Because both chromyl bromide and chromyl iodide are not volatile in nature.

Q. 8.42. For testing SO_4^{2-} with $BaCl_2$ solution, why should sodium carbonate not be acidified with too much of conc. HCl.

Ans. In the presence of conc. HCl, $BaCl_2$ itself will be precipitated. The precipitated $BaCl_2$ is mistaken as $BaSO_4$.

Q. 8.43. Can any other reagent in place of lime water be employed for identification of CO_2 gas ?

Ans. Yes, $Mg(OH)_2$ can be employed.

Q. 8 44. At times in the bottle of nitric acid, brown vapours are seen. Comment.

Ans. Nitric acid decomposes in the presence of light giving NO_2 gas which is brown.

Q. 8 45. Can $Ba(NO_3)_2$ solution in place of $BaCl_2$ be used in the detection of SO_4^{2} ions ?

Ans. Yes. It is the Ba^{2+} ions which forms white ppt. with SO_4^{2-} ions. Both $BaCl_2$ and $BaNO_3$ contain Ba^{2+} ions.

Q 8.46. Sometimes a white ppt. appears when the salt is heated with conc. H_2SO_4. What does it suggest ?

Ans. The salt may have Pb^{2+}, Ba^{2+} or Sr^{2+} ions which on reacting with conc. H_2SO_4 give insoluble sulphates of Pb^{2+}, Ba^{2+} and Sr^{2+}.

Q 8.47. At times the solution of lime water appears milky. Comment.

Ans. The lime water lying in the reagent bottle absorbs CO_2 gas from the atmosphere and produces white insoluble $CaCO_3$.

$$Ca(OH)_2+CO_2 \longrightarrow CaCO_3(s)+H_2O$$

Q 8.48. Name the gas other than CO_2 which also turns lime water milky.

Ans. SO_2 gas also turns lime water milky as insoluble $CaSO_3$ is produced.

Q 8.49. How will you explain the appearance of yellow ppt. with ammonium molybdate in the absence of PO_4^{3-} ion ?

Ans. Phosphate is tested by heating the mixture with conc. HNO_3 and ammonium molybdate when a yellow ppt. of ammonium phosphomolybdate $(NH_4)_3PO_4.12MoO_3$ shows its presence. Arsenic also forms yellow ppt. of ammonium arsenomolybdate under these conditions.

Q. 8.50. Why is necessary to test for the acid radicals first with dilute H_2SO_4 and then with conc H_2SO_4 ?

Ans. There are some ions like, SO_3^{2-}, S^{2-}, NO_2^-, and CH_3COO^- which can react with dilute/conc. H_2SO_4 whereas ions like Cl^-, Br^-, I^-, NO_3^- *etc.* react only with conc. H_2SO_4.

Now if conc. H_2SO_4 is used first then the anions of both the types will react. Hence it is desired to test acid radicals first with dilute H_2SO_4 and then with conc. H_2SO_4.

Q. 8.51. What is chromyl chloride test ? Why is it so named ?

Ans. Chlorides of metals other than heavy ones *e.g* Hg^{2+} on reacting with conc. H_2SO_4 and $K_2Cr_2O_7$ produce orange colour vapours, which on reacting with NaOH and lead acetate produce yellow ppt. of $PbCrO_4$.

Orange colour vapours are that of chromyl chloride, CrO_2Cl_2, hence the test is so named.

Q. 8.52. Sodium carbonate extract is acidified with HNO_3 in the identification of halides. Comment.

Ans. HCl and H_2SO_4 are not used as the acids react with the test reagent $AgNO_3$ and form ppt. of AgCl and Ag_2SO_4 respectively. Because of this only HNO_3 is used for the purpose.

Q. 8.53. Why is it necessary to prepare original solution for the detection of basic radicals ?

Ans. The detection of basic radicals depends on the behaviour of ions in solution. For this purpose the preparation of original solution is necessary as it furnishes free ions in solution.

Q. 8.54. Why do we not prefer to prepare original solution in conc. H_2SO_4 or conc. HNO_3 ?

Ans. It is not advisable to prepare original solution in conc. HNO_3 or conc. H_2SO_4 because these are oxidizing agents and they oxidize H_2S in group II to produce a yellow ppt. of sulphur.

$$H_2SO_4 \longrightarrow H_2O+SO_2+[O]$$

$$HNO_3 \longrightarrow H_2O+NO_2+[O]$$

$$H_2S+O \longrightarrow H_2O+\underset{\text{(Yellow)}}{S(s)}$$

Also Pb^{2+}, Ba^{2+}, Sr^{2+}, Ca^{2+} are precipitated as their insoluble sulphates in presence of conc. H_2SO_4.

$$BaCl_2+H_2SO_4 \longrightarrow \underset{\text{(Insoluble)}}{BaSO_4(s)}+2HCl$$

Q. 8.55. What is solubility product ? Explain its importance in qualitative analysis.

Ans. The ionic product in a saturated solution of an electrolyte at a given temperature is always a constant quantity and is termed as solubility product. This is denoted by symbol S.

Whenever in a solution the ionic product exceeds the solubility product, the precipitation occurs due to the supersaturation of solution.

Q. 8.56. What is the basis of classification of cations into different groups ?

Ans. The different cations are classified under six group depending upon the difference in the solubilities of their chlorides, sulphides, hydroxides and carbonates at different pH values.

Q. 8.57. What should we do if the salt is soluble only in dil. or conc. HNO_3 ?

Ans. Evaporate the solution to almost dryness and then dissolve the residue in water or dil. HCl and proceed for the analysis.

Q. 8 58. Why are only Pb^{2+}, Ag^+ and Hg_2^{2+} ions precipitated in group I ?

Ans. Out of all the chlorides, those of Pb^{2+}, Ag^+ and Hg_2^{2+} are insoluble. HCl is the reagent of group I. Thus, chlorides of Pb^{2+}, Ag^+, and Hg_2^{2+} are precipitated in group I.

$$AgNO_3+HCl \longrightarrow \underset{\text{(White ppt.)}}{AgCl(s)}+HNO_3$$

Other cations remain in solution because their chlorides are soluble.

Q. 8.59. Why is lead placed in group I as well as in II ?

Ans. This is due to fact that lead is not completely precipitated in group I as lead chloride. $PbCl_2$ is also soluble in hot water. Therefore, the lead which escapes precipitation in group I as $PbCl_2$ is precipitated in the group II as PbS.

Q. 8.60. Is it necessary to acidify a solution before group II cations are precipitated with H_2S ?

Ans. Yes, because for the precipitation of cations of group II only small concentration of sulphide ions (S^{2-}) is required.

This condition is achieved by passing H_2S gas in a solution acidified with HCl (dil.). Due to common ion effect, concentration of S^{2-} ions decreases as presence of hydrochloric acid suppresses the ionization of H_2S—resulting only in the precipitation of sulphides of group II metals.

Other metal sulphides remain in solution as they require higher concentration of S^{2-} ions for their precipitation.

Q. 8.61. Why do we prefer HCl for preparing solutions of cations ?

Ans. Because most of the salts are soluble in HCl except those of group I.

Q. 8.62. Why is it essential to boil off H_2S gas before proceeding to group III ?

Ans. Otherwise the sulphides of group IV will also be precipitated along with precipitate of group III.

Q. 8.63. Can the solution be acidified with HNO_3 in place of HCl in group II before passing H_2S gas ?

Ans. No, HNO_3 being oxidizing in nature, oxidizes H_2S gas to form colloidal sulphur, which makes the analysis complicated.

Q. 8.64. Name the precipitate of group I which is soluble in hot water and insoluble in cold water.

Ans. Lead (II) chloride.

Q. 8.65. Give the reason for the formation of a light yellow or white ppt. in the group II even if it may not be because of some metal ion.

Ans. Yellow or white ppt. is formed due to the oxidation of H_2S gas by some oxidizing agents to sulphur which floats on the surface.

$$BaSO_3+2HCl+2H_2S \longrightarrow BaCl_2+3H_2O+\underset{\text{(Yellow)}}{3S}$$

$$2NaNO_3+H_2S+2HCl \longrightarrow 2NO+2NaCl+2H_2O+\underset{\text{(Yellow)}}{S}$$

$$FeCl_3+H_2S \longrightarrow 2FeCl_2+2HCl+\underset{\text{(Yellow)}}{S}$$

Q. 8.66. At times one finds some white ppt. floating on the surface of NaOH solution. Comment.

Ans. NaOH solution reacts with atmospheric CO_3 gas and forms Na_2CO_3 which may float.

Q. 8.67. Is it advisables to use conc. HCl in place of dilute HCl for preparing original solution ?

Ans. Conc. HCl can be used but to ensure the precipitation of Pb^{2+} as $PbCl_2$ the solution is prepared in dil. HCl as $PbCl_2$ dissolves in conc. HCl due to complex formation.

Q. 8.68. What is common ion effect ? Give two examples of common ion effect in qualitative analysis of cations.

Ans. Ionisation of a compound A^+B^- is suppressed by addition of another compound A^+C^- having the common ion, A^+. This is termed the common ion effect. In the third group, ionization of $NH_4OH(NH_4OH \rightleftharpoons NH_4^+ + OH^-)$ is suppressed by adding $NH_4^+Cl^-$ having the common ion, NH_4^+.

In the second group, ionization of $H_2S(H_2S \rightleftharpoons 2H^+ + S^{2-})$ is suppressed by adding HCl having the common ion, H^+.

Q. 8.69. Group I filtrate is made moderately acidic before proceeding to Group II.

Ans. Precipitation of the sulphide can occur only when the ionic product $[M^{2+}][S^{2-}]$ exceeds the solubility product of the sulphide, MS.

In the presence of acid, the ionization of H_2S is suppressed due to the increased concentration of H^+. As a result, there are only few S^{2-} ions in solution which are enough only to precipitate only group II cations as sulphides, *e.g.* CuS, PbS, *etc.*

But for the precipitation of CdS, the coneentration of S^{2-} is not enough. Hence the concentration of $[H^+]$ should be further decreased by diluting the solution so that the H_2S is ionized extensively. As a result S^{2-} ions are made available in sufficient quantity which can precipitate the Cd^{2+} ions, *i.e.*, ionic product $[Cd^{2+}][S^{2-}]$ exceeds the solubility product of CdS.

Q. 8.70. What is the use of adding nitric acid in the precipitation of group III cations as hydroxides.

Ans. Nitric acid is useful in the oxidation of ferrous salts to ferric salts in group III.

$$3FeSO_4+4HNO_3 \longrightarrow Fe_2(SO_4)_3+Fe(NO_3)_3+NO+2H_2O$$

Q. 8.71. Why is it essential to oxidize ferrous salt to ferric salt ?

Ans. This is because the ferrous salts are not completely precipitated as $Fe(OH)_2$ in the presence of NH_4Cl on the addition of NH_4OH and thus iron will also be precipitated in the group IV as FeS on passing H_2S.

Therefore, to precipitate iron completely in the group III, it is necessary to oxidize ferrous salt to ferric salt.

Q. 8.72. Why do we add excess of NH_4Cl and NH_4OH in the precipitation of group III cations ?

Ans. The solubility product of hydroxids of cations of group III is extremely low.

NH_4Cl suppresses the ionization of NH_4OH to a great extent due to common ion effect. As a result, low concentration of OH^- is made available for precipitating group III cations hydroxides.

Other hydroxides remain in solution as they require higher concentration of OH^- ions for pcecipitation as hydroxides.

Q. 8.73. Can NH_4Cl be replaced by any other ammonium salt for the precipitation of group III cations ?

Ans. Yes, NH_4NO_3 can be used in place of NH_4Cl for the precipitation of group III cations. Ammonium sulphate cannot be used as it may precipitate Ca^{2+}, Ba^{2+} and Sr^{2+} as insoluble sulphates.

Q. 8.74. Why are Zn, Mn, Ni, Co not precipitated in the group III as hydroxides ?

Ans. The solubility product of hydroxides of Zn, Mn, Ni and Co is very high. For this purpose they require high concentration of OH^- ions. This is not possible in the group III as NH_4Cl suppresses the ionization of NH_4OH due to common ion effect.

Q. 8.75. How will you distinguish between ferrous and ferric salts ?

Ans. Ammonium sulphocyanide does not give any colouration with ferrous salt while it gives a blood red colour with ferric salt.

Potassium ferricyanide produces a blue ppt. with ferrous salt while a brown colouration is obtained with ferric salt.

Potassium ferrocyanide gives deep blue colour or ppt. with Ac^{3+} ions only.

Q. 8.76. Can we add NH_4OH first and NH_4Cl later in the analysis of group III cations ?

Ans No ; the function of NH_4Cl is to suppress ionization of NH_4OH and thereby prevent precipitation of $Zn(OH)_2$, $Mg(OH)_2$, $Mn(OH)_2$, *etc.*

In case NH_4OH is added first, these hydroxides will be immdiately precipitated. Once hydroxides are precipitated addition of NH_4Cl will be of no use.

Q. 8.77. Can we use NaCl and NaOH in place of NH_4Cl and NH_4OH in the group III cations precipitation ?

Ans. No ; NaOH is a strong base and highly ionized. Even in the presence of NaCl, $[OH^-]$ will be large enough to precipitate $Zn(OH)_2$, $Mg(OH)_2$, *etc.*

Q. 8.78. Why is a brownish ppt. obtained in Group III even if iron, aluminium and chrominium are not present ?

Ans. When NH_4Cl is not present in sufficient amount, Mn is precipitated as $MnO_2.H_2O$ which is brown in colour.

Q. 8.79. Why are the group IV cations not precipitated as sulphides on passing H_2S gas through group II solution ?

Ans. For the precipitation of cations of group IV, a very large concentration of sulphide ions (S^{2-}) is required which is not available in the group II as the ionization of H_2S is suppressed by HCl (common ion effect).

In precipitating the cations of group IV, high concentration of S^{2-} ions is reached as OH^- ions released by NH_4OH unite with H^+ ions given by H_2S. Thus the solubility product is exceeded and the cations of graup IV are precipitated as ZnS, NiS, MnS and CoS.

Q. 8.80. How will you explain the addition of excess of NH_4OH in precipitating the sulphides of group IV cations ?

Ans. The solubility product of Group IV radicals is greater than that of Group II ions. Therefore, a higher concentration of S^{2-} ions is required to precipitate Group IV ions as their sulphides. Now to get a higher concentration of S^{2-} ions, H_2S gas is passed in presence of NH_4OH. The OH^- ions from NH_4OH neutralize the H^+ ions from H_2S to form undissociated water molecules. The removal of H^+ ion causes more H_2S to dissociate or ionize, thus increasing the concentration of S^{2-} ions and so the product $[M^{2+}][S^{2-}]$ exceeds the solubility products of the sulphides of Zn, Mn, Ni and Co and hence they are precipitated.

(M=Zn, Mn, Co or Ni)

$$2NH_4OH \rightleftharpoons 2NH_4^+ + 2OH^-$$

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$$2H^+ + 2OH^- \rightarrow 2H_2O.$$

Q. 8.81. Why is, at times, a black coloured precipitate obtained in group IV even if nickel and cobalt ions are not present ?

Ans. A black coloured precipitate is obtained in the group IV due to the incomplete removal of iron in group III. Iron escapes precipitation in group III due to lack of enough NH_4OH. Fe^{3+} is reduced to Fe^{2+} by H_2S which finally gets precipitates as FeS (black) in group IV even when both Co and Ni are absent.

$$FeCl_2 + H_2S \longrightarrow 2HCl + \underset{\text{(Black ppt.)}}{FeS\,(s)}$$

Q. 8.82. At times colloidal precipitate is obtained in group IV. Comment.

Ans. To prevent the colloidal precipitate, ammonium chloride must be present in large, amount. H_2S should not be passed for long.

Q. 8.83. All aqueous solutions of the cobaltous salts are pink. Comment

Ans. Almost all aqueous solutions of cobaltous salts are pink due to the formation of $[Co(H_2O)_6]^{2+}$ ion.

Q. 8 84. Why is NH_4Cl essential in the precipitation of the group V cations ?

Ans. Ammonium chloride prevents the precipitation of Mg^{2+} as $MgCO_3$ by the group reagent $(NH_4)_2\,CO_3$ by lowering down its dissociation into NH_4^+ and CO_3^{2-} ions.

Q. 8.85. Does the excess of NH_4Cl affect the precipitation of group V cations by $(NH_4)_2\,CO_3$?

Ans. Yes, the concentration of CO_3^{2-} is decreased because the common ion NH_4^+ suppresses the ionization of $(NH_4)_2\,CO_3$.

$$2NH_4^{2+} + CO_3^{2-} \rightleftharpoons (NH_4)_2 CO_3$$

to such an extent that the solubility products of Group V carbonates are not exceeded and therefore they are not precipitated.

Further the concentration is decreased because of the combination of NH_4^+ and CO_3^{2-}.

Q. 8.86. How will you remove the excess of NH_4Cl before adding $(NH_4)_2CO_3$ for the precipitation of Group V ?

Ans. $NHCl_4$ is removed by treating the filtrute from Group IV with couc. HNO_3. On heating to dryness ammonium chloride is decomposed according to the following equations :

$$NH_4Cl + HNO_3 \rightarrow NH_4NO_3 + HCl$$
$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

Q. 8.87. Why is $CaSO_4$ not precipitated on adding ammonium sulphate to a solution containing Ca^{2+} and Sr^{2+} ions ?

Ans. $CaSO_4$ is not precipitated due to the formation of a complex with $(NH_4)_2SO_4$.

$$(CH_3COO)_2Ca + (NH_4)_2SO_4 \rightarrow CaSO_4 + 2NH_4Cl$$
$$CaSO_4 + (NH_4)_2SO_4 \rightarrow \underset{\text{(Soluble complex)}}{(NH_4)_2 [Ca(SO_4)_2]}$$

Q. 8.88. At times NH_4OH is added before adding $(NH_4)_2CO_3$, to precipitate group V cations. Explain.

Ans. Ammonium hydroxide reacts with bicarbonate present as impurity in $(NH_4)_2CO_3$ as given below :

$$NH_4HCO_3 + NH_4OH \rightarrow (NH_4)_2CO_3 + H_2O$$

The presence of bicarbonate is undesirable as the bicarbonates of Ba^{2+}, Sr^{2+} and Ca^{2+} are soluble in water.

Q. 8.89. At times warning is suggested while precipitating group V cations. Explain.

Ans. The impurity of bicarbonate ion in $(NH_4)_2CO_3$, form soluble bicarbonates of Ba^{2+} and Sr^{2+}. Warming decomposes these bicarbonates into normal carbonates which are precipitated.

$$Ca\,(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$

The solution must not be boiled otherwise insoluble carbonates with ammonium chloride are converted into soluble chlorides.

$$CaCO_3 + 2NH_4Cl \rightarrow CaCl_2 + (NH_4)_2CO_3.$$

Q. 8.90. Can we use $Na_2\,CO_3$ in place of $(NH_4)_2CO_3$ in Group V ?

Ans. No ; $(NH_4)_2CO_3$ is a weak electrolyte and its ionization is suppressed by the presence of NH_4Cl. Na_2CO_3 is a strong electrolyte and in its solution $[CO_3^{2-}]$ is pretty high to precipitate even $MgCO_3$ in group V.

Q. 8.91. At times no precipitate is obtained on adding $(NH_4)_2CO_3$ even if Group V radicals are present. Comments.

Ans. Precipitate is obtained when the solution is dilute. In dilute solution, $(NH_4)_2CO_3$ hydrolyses to give carbonic acid which is a weak electrolyte. Its ionization does not produce sufficient CO_3^{2-} ions concentration to precipitate Ca^{2+}, Sr^{2+} and Ba^{2+} as carbonates.

$$(NH_4)_2CO_3+2H_2O \rightarrow 2NH_4OH+H_2CO_3$$

Q. 8.92. Why do we test Group V cations in the order of Ba, Sr and Ba ?

Ans. This order is based on the following facts :

(*i*) Only the chromate of barium is insoluble in acetic acid whereas those of calcium and stontium are soluble in acetic acid.

(*ii*) Both barium and strontium form in soluble sulphates but calcium does not.

(*iii*) The oxalates of barium, strontium and calcium are insoluble.

Q. 8.93. Only acetic acid is employed for dissolving the Group V ppt. Comment.

Ans. It is due to the following reasons :

(*a*) If H_2SO_4 is used, Ba^{2+}, Sr^{2+} and Ca^{2+} will be precipitated as their sulphates.

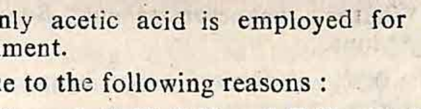
(*b*) If the ppt. is dissolved either of the three acids, *i.e.*, dilute HCl, H_2SO_4 or HNO_3, calcium will not be precipitated by adding $(NH_4)_2C_2O_4$ because CaC_2O_4 formed is soluble in these acids.

However, the use of CH_3COOH is free from the above difficulties. Hence it is used for dissolving the Group V ppt.

Q. 8.94. Calcium oxalate is soluble in dilute HCl ? Explain.

Ans. When calcium oxalate is treated with dil. HCl the oxalate ions will combine with H^+ ions of HCl to give feebly ionized oxalic acid.

$$HCl \rightleftharpoons H^+ + Cl^-$$



$$\begin{array}{l}COO\\|\\COO\end{array}\!\!>Ca^+ + 2H^+ \rightleftharpoons \begin{array}{l}COOH\\|\\COOH\end{array} + Ca^{2+}$$

(Feebly ionized)

Q. 8.95. Why is a precipitate of magnesium carbonate not formed along with the carbonates of Ba^{2+}, Sr^{2+} and Ca^{2+} in group V ?

Ans. Magnesium requires higher concentration of CO_3^{2-} ions for its precipitation as $MgCO_3$ which is insufficient in group V due to the presence of NH_4Cl along with $(NH_4)_2CO_3$.

NH_4Cl suppresses the ionization of $(NH_4)_2CO_3$ thereby a low concentration of CO_3^{2-} ions is made available due to common ion effect.

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$
$$(NH_4)_2CO_3 \rightleftharpoons \underset{\text{(Common ion)}}{2NH_4^+} + \underset{\text{(Low concentration)}}{CO_3^{2-}}$$

Q. 8.96. At times a white ppt. is obtained in Group VI even in the absence of Mg. Comment.

Ans. The cations of Group V which are not completely precipitated, precipitate in Group VI. As a result the ionic product $[Ca^{2+}][C_2O_4^{2-}]$ becomes less than the solubility product of CaC_2O_4 and hence it dissolves in HCl.

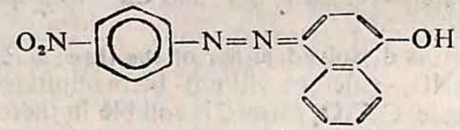
Q. 8.97. How is magnesium identified in Group VI ?

Ans. The filtrate from Group V is treated with disodium hydrogen phosphate and aq. ammonia. A white crystalline ppt. of Mg $(NH_4)PO_4$ is obtained on scratching the walls of test tube.

$$MgCl_2 + Na_2HPO_4 + NH_3 \longrightarrow MgNH_4PO_4 + 2NaCl$$

Q. 8.98. What is a magneson reagent ? Suggest its use in the detection of Mg^{2+} ions.

Ans. It is a 0.5% solution of *p*-nitrobenzene-azo-resorcinol in 0.25N NaOH solution.



p-Nitrobenzene-azo-resorcinol

It is used for testing Mg^{2+} ions. Magneson reagent is added to the filtrate obtained from Group V. A blue lake is formed when the mixture is made alkaline with NaOH

With NaOH, Mg^{2+} ions present in the Group V filtrate from a ppt. of magnesium hydroxide.

$$Mg^{2+} + 2OH^- \longrightarrow Mg(OH)_2$$

On the ppt. of $Mg(OH)_2$, magneson dye is adsorbed to yield a blue coloured lake.

$$\text{Magneson} + Mg(OH)_2 \longrightarrow \text{Blue lake}$$

□ □

UNIT 9

Identification of Ions in Common Fertilizers

9.1. INTRODUCTION

Increasing population is putting strains on the food resources of this planet. Chemistry plays a very important role in the development of agriculture and in the production of more and better food. Chemical fertilizers or manures are added to the soil to increase its fertility as for the healthy growth of plants. The production of food stuffs today owes much not only to the use of chemical fertilizers but also to the development of selective weed killers and pesticides.

In the 1840s, Liebig, a German chemist, analyzed bird droppings and found that nitrogen, phosphorus and potassium formed the three major components. Experiments quickly confirmed that plants produced unprecedented yields when treated with bird droppings. Thus, the 'N-P-K' theory of fertilization was born.

These three elements, *i.e.* nitrogen, phosphorus and potassium are the primary or macro-nutrients. These are used up by plants and the soil suffers a deficiency of compounds of these elements in soil. Apart from these, iron, calcium, magnesium and sulphur, called secondary nutrients, (micro-nutrients) are also required in small quantities. Later it was discovered that elements like, cobalt, zinc, molybdenum, copper mangenese, chlorine and boron play key roles in plant nutrition. Their deficiency in soil is less common.

A manure is a natural substance obtained by the decomposition of animal excreta or plant residues. A chemical fertilizer is an artificially produced salt or some other chemical substances (organic or inorganic) containing the necessary plant nutrients. The elements are present in such forms that plant can readily make use of them. Manures contain plant nutrients in small amounts but organic matter such as humus in plenty as compared to fertilizers. Humus increases the productive capacity of the soil. It improves the physical and chemical properties of the soil.

Some of the common fertilizers are listed below :

1. **Nitrogenous fertilizers.** Ammonium sulphate, ammonium nitrate, sodium nitrate, urea, calcium cyanamide, calcium ammonium nitrate (CAN).

2. **Phosphatic fertilizers.** Superphosphate of lime or triple superphosphate.

3. **Potassium or potash fertilizers.** Potassium chloride, potassium nitrate.

Fertilizers, which contain only one primary nutrients (*i.e.* N, P or K) are called **single fertilizers**. Fertilizers composed of more than one primary nutrients are known as **mixed fertilizers.** According to the contents, they are classified as NK, NP, PK or NPK type. For example,

(*i*) Potassium nitrate, KNO_3—A fertilizer of NK type

(*ii*) Ammonium dihydrogen phosphate, $(NH_4)H_2PO_4$—A fertilizer of NP type (Ammophos)

NPK type fertilizers are called complete fertilizers. They supply all the primary nutrients.

9.2. IDENTIFICATION OF IONS IN COMMON FERTILIZERS

Most of the known common fertilizers contain NH_4^+, Ca^{2+}, K^+, Na^+, NO_3^-, SO_4^{2-}, Cl^- and PO_4^{3-} ions which can easily be detected in their aqueous solutions by the usual tests of these ions discussed in Unit 8.

Table 9.1. Identification of Cl^- and NO_3^- ions

Experiment	*Observation*	*Inference*
1. Take a small quantity (0.5 g) of the fertilizer in a test-tube and add conc. H_2SO_4 (1 mL). Observe if any reaction takes place in cold. Warm gently and observe the gas evolved.	(*i*) Pungent smelling and irritating gas (due to evolution of HCl) (*ii*) Light brown fumes with a characteristic irritating smell (due to NO_2 gas)	Cl^- present NO_3^- present
2. If a pungent smelling gas evolves		
(*i*) bring a glass rod carrying a drop of amomnia solution near the issuing gas.	Dense white fumes of NH_4Cl are produced	Cl^- present
(*ii*) add a small amount of MnO_2 to the reaction mixture and heat it.	Greenish yellow Cl_2 gas evolves. It has a pungent odour.	Cl^- present
(*iii*) bring moist iodized starch-paper near the opening of the test-tube in (*ii*).	Dark blue colour appears.	Cl^- present

3. (i) Acidify 1 mL of aqueous solution of fertilizer with dilute HNO_3 and add $AgNO_3$ solution.	Dirty white ppt. of AgCl appears which turns grey on getting exposed to light.	Cl^- confirmed
(ii) Add aqueous ammonia to the white ppt. of AgCl.	ppt. dissolves forming a soluble complex	Cl^- confirmed
4. **Chromyl Chloride Test :** Take 0.5 g of the fertilizer (1 part) and $K_2Cr_2O_7$ (1 part) in a test tube. Add conc. H_2SO_4 and heat.	Red vapours of chromyl chloride are produced.	Cl^- confirmed
Pass the red vapours of CrO_2Cl_2 through dil. NaOH solution.	Yellow solution of sodium chromate is obtained.	Cl^- confirmed
Acidify the yellow solution with acetic acid and add lead acetate solution.	Yellow ppt. of lead chromate is obtained	Cl^- confirmed
5. If the fertilizer on reacting with conc. H_2SO_4 produces light brown fumes		
(i) add copper turnings to the reaction mixture and heat.	Dense brown fumes evolve.	NO_3^- present
(ii) expose a moist potassium iodide paper to the issuing fumes	The paper acquires yellow colour.	NO_3^- present
(iii) expose a moist iodized starch paper to the issuing fumes.	The paper acquires a blue colour.	NO_3^- present
6. To aqueous solution of fertilizer add freshly prepared ferrous sulphate solution followed by conc. H_2SO_4 along the side of the tube.	Conc. H_2SO_4 forms the bottom layer. A brown ring appears at the junction of the two liquids due to the formation of complex.	NO_3^- present

Table 9.2. Identification of SO_4^{2-} and PO_4^{3-}

Experiment	*Observation*	*Inference*
1. Acidify 2-3 mL of aqueous solution of fertilizer with dil. HCl and divide the solution in two parts.		
(i) To one part add barium chloride solution.	White ppt. of $BaSO_4$ is obtained. Insoluble in all mineral acids.	SO_4^{2-} confirmed
(ii) To the other part of the solution add acetic acid and lead acetate solution	White ppt. of lead sulphate is obtained which is soluble in ammonium acetate solution, due to the formation of soluble lead acetate.	SO_4^{2-} confirmed

2. Acidify 2-3 mL of aqueous solution of fertilizer with dil. HNO_3. To this add 2-3 mL of conc. HNO_3 and 5 mL of ammonium molybdate solution. Now heat the contents.	Slow formation of canary-yellow ppt. of ammonium phosphomolybdate takes place.	PO_4^{3-} present

The chemistry involved in the tests performed (Tables 9.1 and 9.2) to identify Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} ions is outlined at the appropriate place in Unit 8.

Table 9.3. Identification of Ca^{2+}

Experiment	*Observation*	*Inference*
1. Perform flame test with the sample of the fertilizer. (For flame test refer to Unit 8).	A brick red flame is obtained.	Ca^{2+} present
2. To the aqueous solution of the fertilizer add $NH_4Cl(aq)$, NH_4OH and $(NH_4)_2CO_3(aq)$ and stirr the contents. Warm and allow to stand the solution.	White ppt. of $CaCO_3$ obtained.	Ca^{2+} present
3. Take the ppt. (from test 2) and add hot dilute acetic acid. To the solution add conc. ammonium oxalate solution and heat.	A white ppt. of calcium oxalate is obtained.	Ca^{2+} confirmed
4. Add to the ppt. (from test 3) obtained, dil. H_2SO_4 or HCl. Now add a few drops of dilute $KMnO_4$ solution.	Pink colour of $KMnO_4$ solution is discharged.	Ca^{2+} confirmed

Table 9.4. Identification of NH_4^+, K^+ and Na^+ ions

Experiment	*Observation*	*Inference*
1. (*i*) Heat a small amount of fertilizer with a few mL of sodium hydroxide solution.	Ammonia gas evolves.	NH_4^+ present
(*ii*) Bring a glass rod dipped into hydrochloric acid near the exit of gas.	Dense white fumes of ammonium chloride are obtained.	NH_4^+ confirmed

2.	To the aqueous solution of fertilizer, add a few drops of NaOH to make it alkaline. Now add 1-2 mL of Nessler's reagent solution.	A brown ppt. (iodide of Millon's base) is obtained.	NH_4^+ confirmed
3.	To 1-2 mL of the aqueous solution of the fertilizer add a few drops of acetic acid and freshly prepared solution of sodium cobaltinitrite. Shake and allow it to stand.	A bright yellow ppt. of $K_2Na[Co(NO_6)]$ is obtained.	K^+ present
4.	Preform the flame test with the solid sample of fertilizer.	A violet flame but intense violet red (or crimson) through blue glass.	K^+ confirmed
5.	To 1-2 mL of the aqueous solution of fertilizer add a small volume of potassium dihydroantimonate (KH_2SbO_4) solution. Warm the solution and scratch the inside of the test tube with a glass rod.	A crystalline white ppt. of NaH_2SbO_4 which sticks to the wall of the test tube.	Na^+ present
6.	Perform the flame test with the solid sample of the fertilizer.	A golden yellow flame but invisible through blue glass.	Na^+ confirmed

Note : While performing the tests of K^+ and Na^+, ammonium salts should be absent as they tend to interfere in their detection.

The chemistry involved in the tests (Table 9.3) performed for identifying Ca^{2+} is given at the appropriate place in Unit 8.

The chemistry involved in the detection of NH_4^+, K^+ and Na^+ is given below :

1. (*i*) Ammonium salt on heating with sodium hydroxide gives ammonia gas.

$$NH_4Cl + NaOH \longrightarrow NaCl + H_2O + \underset{\text{Ammonia}}{NH_3(g)}$$

(*ii*) Ammonia gas reacts with the vapours of HCl forming dense white fumes of ammonium chloride.

$$NH_3 + HCl \longrightarrow \underset{\text{(Dense white fumes)}}{NH_4Cl(s)}$$

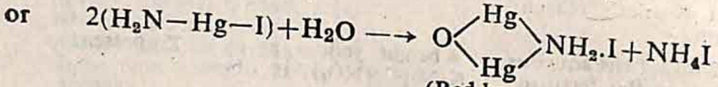
2. Alkaline solution of ammonium salt reacts with Nessler's reagent. A red brown ppt. of the iodide of Million's base, $NH_2Hg_2I_3$ is obtained.

$$NH_4^+ + NaOH \longrightarrow NH_3 + H_2O + Na^+$$

$$\underset{\text{Nessler's reagent}}{K_2HgI_4} \longrightarrow 2KI + HgI_2$$

$$HgI_2+2NH_3 \longrightarrow Hg(NH_2)I+NH_4I$$

$$Hg(NH_2)I+HgI_2 \longrightarrow \underset{\text{(Red brown ppt.)}}{NH_2Hg_2I_3(s)} \text{ or } [Hg_2I_2NH_2]I$$



or $2(H_2N-Hg-I)+H_2O \longrightarrow O\begin{matrix}Hg\\Hg\end{matrix}NH_2.I+NH_4I$

(Red brown ppt.)

3. Addition of sodium cobaltinitrite to a solution containing K^+ ions gives a yellow crystalline ppt. of potassium sodiocobaltinitrite.

$$2KCl+Na_3[Co(NO_2)_6 \longrightarrow K_2Na[Co(NO_2)_6+2NaCl$$

The precipitation reaction is also shown by NH_4^+ ions. Hence the test for K^+ ions should be performed in the absence of NH_4^+ ions. If NH_4^+ ions are present they should be removed from the solution by boiling it with Na_2CO_3 or NaOH before performing the test.

4. The chemistry of the flame test has already beer discussed in Unit 8.

5. Weakly alkaline or neutral solution of sodium compounds when treated with a solution of potassium dihydroantimonate gives a white crystalline ppt. of sodium dihydroantimonate.

$$NaNO_3+KH_2SbO_4 \longrightarrow \underset{\text{(White)}}{NaH_2SbO_4(s)}+KNO_3$$

6. The chemistry of the flame test has already been discussed in Unit 8.

ORAL QUESTIONS AND ANSWERS

Q. 9.1. What is a fertilizer ?

Ans. A chemical compound which is added to the soil for making up the deficiency of primary plant nutrients.

Q. 9.2. How does a manure differ from fertilizer ?

Ans. A manure is a natural substance whereas a fertilizer is synthetic chemical compound.

Q. 9.3. Name the groups of chemical fertilizers.

Ans. 1. Nitrogenous fertilizers.
2. Phosphatic fertilizers.
3. Potash fertilizers.

Q. 9.4. Name three nitrogenous fertilizers with their ormulae ?

Ans. 1. Sodium nitrate ($NaNO_3$).
2. Ammonium nitrate (NH_4NO_3).
3. Calcium ammonium nitrate (CAN) ; $CaNH_4(NO_3)_3$.

Q. 9.5. What are the primary nutrients ?

Ans. Elements needed by plants in large amounts are called primary nutrients, *e.g.* Nitrogen, phosphorus and potassium.

Q. 9.6. Name three secondary nutrients.

Ans. Calcium, magnesium and iron.

Q. 9.7. What are mixed fertilizers ?

Ans. Mixed fertilizers are those which provide more than one primary nutrients to the soil, *e.g.* Calcium ammonium nitrate (CAN).

Q. 9.8. Name the most important phosphatic fertilizer.

Ans. Superphosphate of lime (a mixture of calcium dihydrogen phosphate and calcium sulphate, which is soluble in water).

Q. 9.9. What is ammophos ?

Ans. It is a NP type fertilizer and its chemical name is ammonium dihydrogen phosphate, $NH_4.H_2PO_4$.

Q. 9.10. What are the essential characteristics of a good fertilizer ?

Ans. 1. It should be soluble in water.

2. It should be stable.

3. The elements present should be easily assimilated by plants.

□ □

UNIT 10

Reactions of Carbohydrates, Fats and Proteins and their detection in Food Stuffs

10.1. INTRODUCTION

Body can be thought of as analogous to a large chemical factory in which many raw materials in the form of food are introduced and converted into useful products to :

(*i*) sustain life, (*ii*) provide energy, (*iii*) promote growth of body, tissues and cells, (*iv*) replace worn out tissues, and (*v*) maintain and regulate body's complex processes, *e.g.* digestion, respiration, metabolism, *etc.*

The essential constituents of a balanced food are water, carbohydrates, proteins, fats and oils (lipids), mineral salts and vitamins. Each of the constituents has specific purpose of function.

10.2. CARBOHYDRATES

This class of compounds are among the most major constituents of most living systems ; act as the main source of energy for biological processes as well as a structural component in plants. In plants, they form the greater part of the cell tissue on which the plant relies for its support. They include familiar substances like glucose, sucrose, starch, cellulose, *etc.* They provide with all the three basic needs of life, *viz.* food (as starch containing grains) clothing and shelter (cellulose in the form of cotton, linen, wood, *etc.*). The name originates from the fact that many sugars (which form parts of this class of compounds) have the general formula $C_n(H_2O)_m$—*i.e.*, carbon hydrate—hence the name carbohydrates. Thus, glucose, $C_6H_{12}O_6$ the most common sugar, can be written as $C_6(H_2O)_6$ and sucrose as $C_{12}(H_2O)_{11}$. However, these representations do not explain their relative nature. They bear little or no relationship to the structures known today.

They are produced by green plants (by chlorophyll, the green pigment of plants) in nature from carbon dioxide and water by the action of sunlight via a process called photosynthesis. Thus, carbohydrates are the end products of photosynthesis in plants.

$$nCO_2 + {}_mH_2O + \text{Solar energy} \longrightarrow \underset{\text{Carbohydrate}}{C_n(H_2O)_m} + nO_2$$

or
$$6CO_2 + 6H_2O \xrightleftharpoons[\substack{\text{Animal respiration} \\ \triangle H = -2860 \text{ kJ mol}^{-1}}]{\substack{\text{Plant photosynthesis} \\ h\nu \text{ (chlorophyll)}}} C_6H_{12}O_6 + 6O_2$$

The driving force for the reaction is supplied by sunlight. **This reaction helps in storing some of the energy given out by the sun.** Animals consume the carbohydrates and convert them back to carbon dioxide and water, in the process releasing and using the stored energy of the sunlight.

Carbohydrates are usually defined as polyhydroxy aldehydes (*e.g.* glucose) and ketones (*e.g* , fructose) or substances that hydrolyse to yield polyhydroxy aldehydes and ketones.

Carbohydrates containing an aldehyde group are collectively called '**aldoses**', while the ketonic sugars are referred to as '**ketoses**'. Thus, glucose is referred to as an **aldohexose** while fructose is an example of **ketohexose** (both glucose and fructose contain six carbon atoms and individual sugars end in the suffix-'ose', hence the name hexose). We have seen that because carbohydrates contain $>C=O$ and $-OH$ groups, they exist, primarily, as **hemiacetals** and **acetals** or as **hemiketals** and **ketals** (Unit 16 Text Book Class XII).

The simplest hydrolysed products of carbohydrates are called **monosaccharides.** They cannot be further hydrolysed into simple carbohydrates. On a molecular basis, carbohydrates that yield on hydrolysis only two molecules of a monosaccharide are called **disaccharides** (*e.g.* maltose and sucrore) ; those that yield three molecules of a monosaccharide are termed **trisaccharides** ; and so on. At times, all such carbohydrates that produce 2 to 10 molecules of a monosaccharide on hydrolysis are called **oligosaccharides.** Carbohydrates that yield a large number of molecules of a monosaccharide (more than 10) are called **polysaccharides** *e.g.*, starch, glycogen and cellulose.

10.2.1. Tests for Sugars

Some of the common tests for carbohydrates are discussed briefly here :

1. **Molisch's test :** This test is given by all types of carbohydrates. To about 1 mL of a 5% aqueous solution of the carbohydrate add 2-3 drops of Molisch's reagent (10% alcoholic solution of α-naphthol). Now add 1-2 mL of conc. H_2SO_4 along the sides of the test tube so that it forms a separate layer. Appearance of blue or violet coloured layer at the junction of two layers shows the presence of a carbohydrate.

Chemistry of the test : Conc. H_2SO_4 reacts with the carbohydrate to form furfural or a derivative of furfural. This unites with α-napthol forming coloured compounds.

2. **Reduction reactions of carbohydrates.** Carbohydrates act as reducing agents. They react with some of the common reagents such as Fehling's solution, Barford's reagent, Benedict's reagent, *etc.* A few disaccharides, *e.g.* sucrose, maltose, *etc.* and polysaccharides do not react with the above listed reagents.

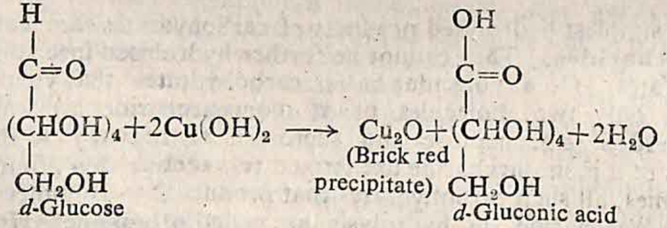
(*i*) **Fehling's solution.** It is a mixture of solution A and and B.

Solution A : It is a 7% aqueous solution of copper sulphate.

Solution B : It is prepared by dissolving ~ 35 g of Rochelle salt (sodium potosium tartrate) and 12 g of caustic soda in 100 mL water. Fehling's solution is prepared by adding equals volumes of both A and B solutions just before the use.

Now to about 1-2 mL of a 5% aqueous solution of carbohydrate add 1-2 mL of Fehling's solution. Heat the content in a boiling water both for ~ 5 min. Apprearance of red ppt. shows the presence of reducing sugars.

Chemistry of the test : Fehling's solution contains Cu^{2+} ions which are reduced to Cu^{+} by carbohydrates. Cu^{+} ions in the alkaline medium are precipitated as cuprous oxide (red colour).



$$\begin{array}{c} H \\ | \\ C{=}O \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} + 2Cu(OH)_2 \longrightarrow \underset{\text{(Brick red precipitate)}}{Cu_2O} + \begin{array}{c} OH \\ | \\ C{=}O \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} + 2H_2O$$

d-Glucose

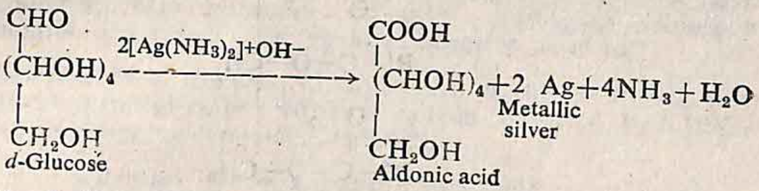
d-Gluconic acid

(*ii*) **Benedict's solution** : To 1-2 mL of a 5% aqueous solution of glucose or lactose in a test tube add 2 mL of Benedict's reagent. Heat the test tube in a boiling water bath. Appearance of a yellow or red ppt. confirms the presence of glucose or lactose.

Chemistry of the test : The chemistry of the test is almost similar to Fehling's solution. Cu^{2+} ions present in the Benedict's solution are reduced o Cu^{+} ions which in the presence of alkali precipitate as cuprous oxide (red).

(*iii*) **Tollen's reagent** : To 1-2 mL of aqueous solution of carbohydrate in a test-tube, add 2-3 mL of Tollen's reagent (ammoniacal silver nitrate solution). Heat the test-tube in a boiling water bath for 5—10 minutes. Appearance of shining silver mirror shows the presence of reducing sugar.

Chemistry of the test : The diammine silver (I) ion present in Tollen's reagent is reduced on treating with glucose (aldohexose) to metallic silver within a few minutes. Sugar is oxidized to aldonic acid.



$$\begin{array}{l}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\\ d\text{-Glucose}\end{array} \xrightarrow{2[Ag(NH_3)_2]^+OH^-} \begin{array}{l}COOH\\ |\\ (CHOH)_4\\ |\\ CH_2OH\\ \text{Aldonic acid}\end{array} + \underset{\substack{\text{Metallic}\\ \text{silver}}}{2\ Ag} + 4NH_3 + H_2O$$

3. **Iodine test** : This test is applicable for starch To an aqueous suspension of starch in water, add a few drops of 0.02 N iodine solution. Appearance of violet purple colour shows the presence of starch.

Chemistry of the test : Iodine forms a blue complex with starch. It is a very specific test for starch.

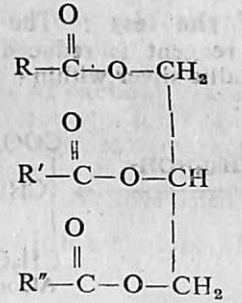
Distinction among common carbohydrates

	Test	*Glucose*	*Lactose*	*Sucrose*	*Starch*
1.	Taste	Sweet	Sweet	Sweet	Tasteless
2.	Solubility in water	Soluble	Soluble	Soluble	Insoluble
3.	Molisch's test	Purple ring	Purple ring	Purple ring	Purple ring
4.	Fehling's reagent	Red ppt.	Red ppt.	Negative	Negative
5.	Benedict's reagent	Red ppt.	Red ppt.	Negative	Negative
6.	Tollen's reagent	Silver mirror	Silver mirror	Negative	Negative
7.	Iodine test	Negative	Negative	Negative	Violet colour

10.3. FATS AND OILS

Fats and oils are esters of gylcerol (a trihydroxy alcohol) and long chain carboxylic acids. These long chain carboxylic acids having even number of carbon atoms are called fatty acids because they occur in fats which are stored in animals and plants. The tri-esters of fatty acids with glycerol are known as triglycerides.

Fats (solids) and oils (liquids) may be represented by the general formula.



Where R, R′ and R″ may be the same or different groups, and the fatty acid parts $(-\overset{\overset{O}{\|}}{C}-R)$ may be saturated or unsaturated. Fats are the esters of glycerol and generally saturated acids. Oils are esters that are produced primarily from unsaturated acids and glycerol The acid part of the fats generally contain an even number of carbon atoms (usually 16 to 18). The acids generally present in fats and oils are

Name	*Structural formula*
Palmitic	$CH_3(CH_2)_{14}COOH$
Stearic	$CH_3(CH_2)_{16}COOH$
Oleic	$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COOH$
Linoleic	$CH_3(CH_2)_4CH=CH-CH_2-CH=CH-(CH_2)_7-COOH$
Linolenic	$CH_3CH_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH-(CH_2)_7COOH$
Ricinoleic	$CH_3(CH_2)_5CH(OH)CH_2-CH=CH(CH_2)_7COOH$

Naturally occurring fats and oils at times contain different kinds of esters. Milk, ghee, butter, and tallow are some of the familiar fats. Peanut oil, olive oil, soyabean oil, cotton seed oil, palm oil and coconut oil are some of the commonly used oils.

10.3.1. Tests for Fats and Oils

1. **Solubility Test**. Fats and oils are soluble in organic solvents such as chloroform, benzene, *etc*. They are insoluble in water. Take a small amount of the fat sample and shake it well with about one mL of chloroform. If it dissolves, the sample may be a fat.

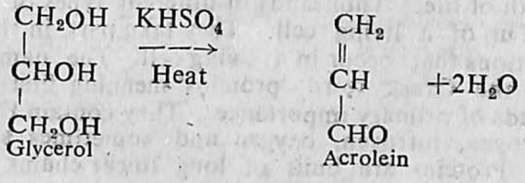
2. **Spot tests for fats and oils**. Place a drop of oil say cottonseed oil on a piece of filter paper. Press it between the folds of the filter paper. If a transluscent spot is formed on the filter paper, it shows the presence of fat or oil.

Heat the filter paper bearing the spot by keeping it slightly away from the flame. If the size of the spot on the filter paper increases, this establishes the presence of fat or oil.

3. **Acrolein test.** Heat a small amount of fat or oil with potassium bisulphate crystals in a test-tube. A pungent odour due to formation of acrolein confirms the presence of fat or oil.

Chemistry of the test. In this reaction, the fat initially gets hydrolysed to free glycerol. Glycerol is then converted by $KHSO_4$ to a pungent smelling compound, aerolein.

$$\text{Oil or fat} \longrightarrow \text{Glycerol} + \text{Fatty acid}$$



$$\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix} \xrightarrow[\text{Heat}]{KHSO_4} \begin{matrix} CH_2 \\ \| \\ CH \\ | \\ CHO \end{matrix} + 2H_2O$$

Glycerol

Acrolein

4. **Distinction between desi ghee and vanaspati ghee.** Vanaspati ghee contains 5% **seasame oil** which is added at the time of manufacture. Pure desi ghee does not contain seasame oil. The detection of seasame oil can be helpful in differentiating pure ghee from vanaspati ghee. Baudouin test is employed for the purpose.

Baudouin's test. Take 1 mL of desi ghee in a test tube and add 1 mL of conc. HCl. Now add a few drops of 2% alcoholic solution of furfural. Shake the contents and keep it for 5-10 min. Appearance of rose red colour confirms the presence of vanaspati ghee in pure desi ghee.

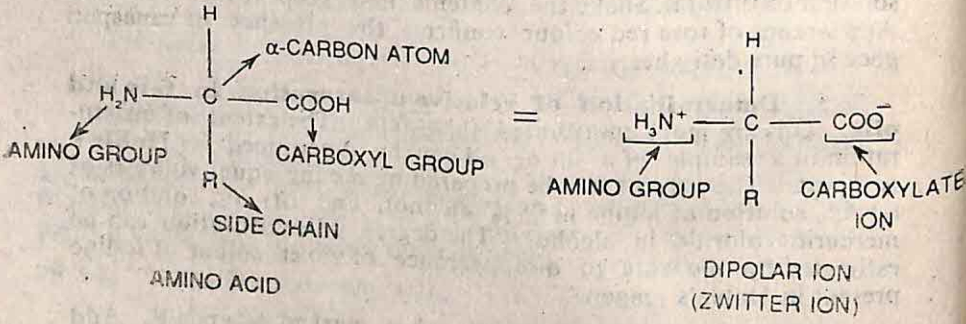
5. **Determination of relative unsaturation in fats and oils.** Oils are more unsaturated than fats. The extent of unsaturation in a sample of a fat or oil can be determined by **Huble's reagent**. The reagent can be prepared by mixing equal volumes of (*i*) 5% solution of iodine in 95% alcohol, and (*ii*) 6% solution of mercuric chloride in alcohol. The degree of unsaturation can be estimated by the rate of disappearance of violet colour of iodine present in Huble's reagent'.

Put 5 mL chloroform in test tubes marked A and B. Add 5-10 drops of the oils say cottonseed and linseed oils in test-tubes A and B respectively. Shake the contents well. Now add 5 drops of the Houble's reagent to each of the test tubes. Look for the relative discharge of iodine colour in the test tubes from time to time. In the tube A having cottonseed oil, the colour of iodine is not discharged whereas in the tube B having linseed oil, the colour of iodine decreases to an appreciable extent. This shows that linseed oil contains a large excess of unsaturated acid.

10.4. PROTEINS

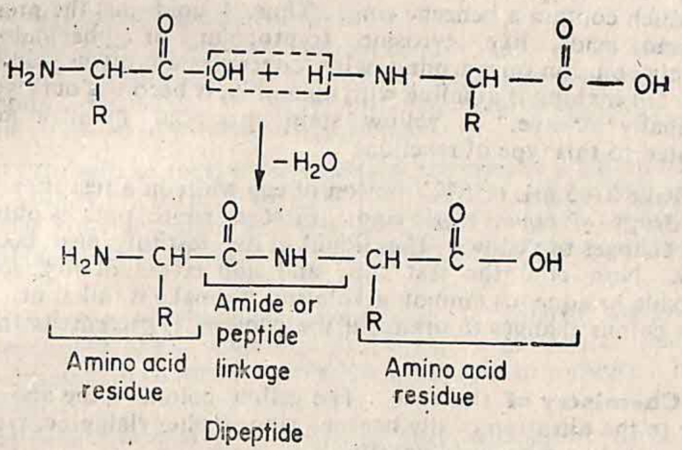
Proteins perform the most diverse functions. As enzymes and hormones, they sustain life by catalyzing and regulating the reactions that occur in the body; as muscles they supply power for movement, as skin and hair they give it a protective covering; as heamoglobins they help in supplying oxygen to all parts of the body; as antibodies they fight against diseases and in combination with other substances in bone they give structural support to the body. Proteins are gigantic polymeric macromolecules of amino acids with high molecular mass produced in plants and animals. They are considered to be the building units of all vegetable and animal bodies. Proteins are essential part of the diet and are vital for the maintenance and growth of life. Thousands of different types of proteins go into the make up of a living cell. They take part in thousands of chemical reactions that occur in a living cell. The name protein is derived from the Greek word 'proteios' meaning first or primary, *i.e.* compounds of primary importance. They contain the elements-carbon, hydrogen, nitrogen, oxygen and sometimes sulphur and phosphorus. Proteins are built of long linear chains of some 20 different α-amino carboxylic acids. Thus, proteins can be termed the polyamides from amino acids (monomeric units).

Although there are structural differences among the common amino acids, there are also certain similarities. They all contain an amino and a corboxyl groups attached to the same carbon atom and are designated α-amino acids. They all differ in the chemical nature of side chain, R. The general formula of an amino acid is given below :



(R = HYDROGEN OR OTHER GROUPS)

Amino acid units are linked together by condensation reaction involving the loss of a water molecule between each joined unit. The α-carboxyl group of one amino acid and the α-amino group of another join through amide linkage, —CO—NH— called peptide linkage. The resulting structures are called peptides. The individual amino acid of a peptide is called amino acid residue.



Depending on the number of amino acid residues per molecule, peptides are referred to as dipeptides, tripeptides and so on finally polypeptides. A protein molecule is a polypeptide and may contain hundreds or thousands of amino acid units joined in a linear fashion. Their molecular masses range from 15000 to 60000 or more Each polypeptide can have any number of any one or the different types of amino acids which can be present in any squence. Each polypeptide has one free carboxylic acid (—COOH) at one end which is called C-terminal and free amino group at the other terminal which is called N-terminal.

On hydrolysis proteins break down into smaller fragments called peptides which in turn hydrolysc to amino acid units.

10 4.1. Tests for Proteins

Colour Reactions of Amino Acids

1. **Biuret test.** A protein solution with alkaline copper sulphate solution gives a violet—pink colour. It serves to identify the presence of protein and polypeptides. To 2—3 mL solution of 5% egg white (or gelatin) in a test-tube, add 1 mL of 40% sodium hydroxide solution. Then add 1—2 drops of 1% copper sulphate solution. Appearance of violet or pink colour shows the presence of proteins.

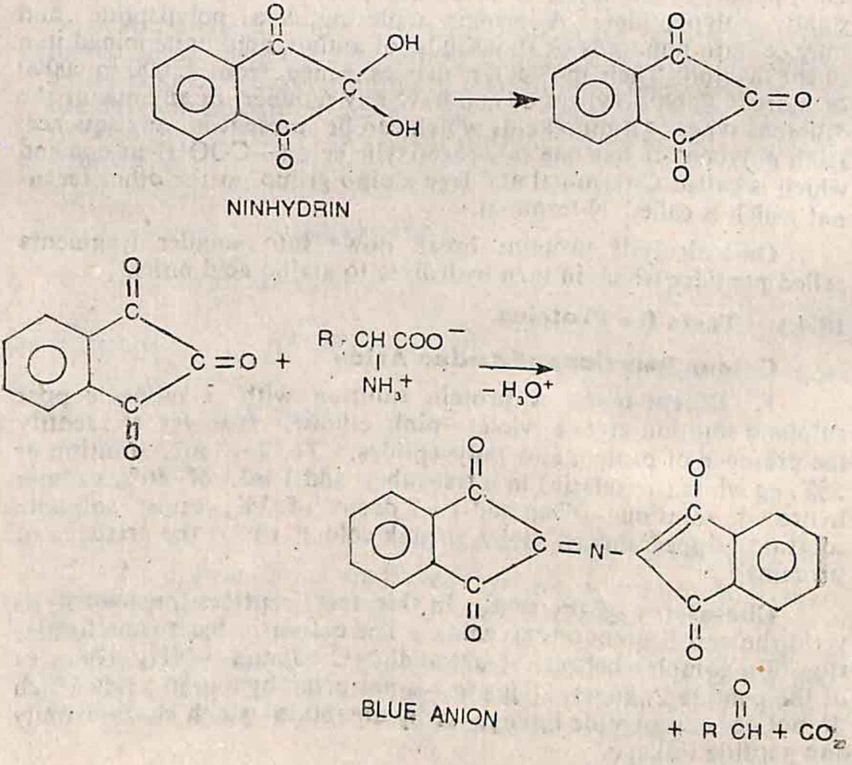
Chemistry of the test. In this test, peptides on hydrolysis yield the constitutent amino acids. The colour is due to the formation of a complex between Cu^{2+} and $>C=O$ and $-NH_2$ groups of of the peptide linkages. This test is not given by amino acids which do not contain peptide linkage or by dipeptide which contains only one peptide linkage.

2. **Xanthoproteic test.** It identifies the presence of amino acids which contain a benzene ring. Thus, it confirms the presence of amino acids, like, tyrosine, tryptophan or phenylalanine. A protein solution on warming with concentrated nitric acid turns yellow. On making it alkaline with ammonia, it becomes dark yellow and finally orange. A yellow stain produced by nitric acid is attributed to this type of reaction.

Take 2—3 mL of 5% solution of egg white in a test tube. Add 2—3 drops of conc. nitric acid. First a white ppt. is obtained which changes to yellow. The liquid in the test tube also becomes yellow. Now cool the test tube and add excess of 40% sodium hydroxide or aqueous ammonia solution to make it alkaline. The yellow colour changes to orange if the protein is present in the egg white.

Chemistry of the test. The yellow colour in the above test is due to the nitration of the benzene ring in phenylalanine, tyrosine and tryptophan present in protein.

3. **Millon's test.** A protein solution with Millon's reagent ($HgNO_3$ in HNO_3) gives a white precipitate which turns brick red



on boiling. It serves to identify proteins which contain the phenolic amino acid, *e.g.* tyrosine. serine, etc.

Add 2−3 mL of Millon's reagent to 2−3 mL of 5% solution of egg white contained in a test tube. Heat the contents in a water both. Formation of white ppt. which turns red on heating shows the presence of protein in egg white.

4. **Ninhydrin test**. It identifies the presence of α-amino acids. Add 4−5 drops of 0·1% ninhydrin solution to mL of 5% solution of egg white contained in a test tube. Boil the contents for one min. Appearance of blue colour on cooling shows the presence of protein.

Chemistry of the test. Ninhydrin, a powerful oxidizing agent, deaminates the α-amino acids liberating ammonia. Deaminated α-amino acid in turn reacts with ninhydrin to produce a blue compound.

Proline and hydroxyproline do not react with ninhydrin in the some way because their α-amino groups are part of a five membered ring.

10.5. EXPERIMENTS

Experiment 10.1. To prove the presence of carbohydrate (glucose) in grapes.

Apparatus. Test tubes, test tube-stand, pestle and mortar, glass rod, funnel, filter paper.

Materials. Grapes, Molisch's reagent, Fehling's solutions, Benedict's reagent, distilled water.

General. If glucose is present in grapes then their juice should give +ve test for carbohydrates (Section 10.2.1).

Procedure. (*i*) Crush some groups in a mortar with pestle. Filter the juice, if necessary. (Juice can be extracted in a electric machine).

(*ii*) Apply various test given for carbohydrates, *i.e.* Molisch's test, Fehling's solution test and Benedict's test, *etc.* using a 1.0 ml. of the juice at a time.

(*iii*) Record the observations of tests in your record book as suggested below :

Obesvations :

Experiment	*Observation*	*Inference*
Extract the juice of grapes. Perform the following tests with juice :		
(*i*) One mL of the juice +Fehling's solution, warm.	Red ppt appears	Carbohydrate present.
(*ii*) ....+Molisch's reagent	....	....
(*iii*) ....+Benedict's solution	....	....

Result. Grapes contain carbohydrates.

Experiment 10.2. To prove the presence of starch in potatoes, banana, corn cobs or sweet potatoes.

Apparatus. Same as in Experiment 10.1.

Materials. Potatoes, *etc.* iodine solution, distilled water.

General. Starch, carbohydrate gives the test with iodine solution (Section 10.2.1).

Procedure. (*i*) Take a few slices of potatoes. Crush them in a mortar with pestle. Add a few mL of distilled water and mix the contents well. Separate the juice.

(*ii*) To 1 mL of potatoes' juice, add a few drops of iodine solution. Observe the colour change. Appearance of blue colour shows the presence of starch.

Apply the same procedure to banana, corn cobs or sweet potatoes.

Result. Potatoes, *etc.* contain starch.

Experiment 10·3. To prove that groundnuts contain oils.

Apparatus. Same as in Experiment 10.1.

Materials. Raw groundnuts, filter paper, potassium bisulphate, distilled water.

Procedure. (*i*) Crush the groundnuts in a mortar with a pestle well and separate the oil. Press the crushed paste of the groundnuts between the folds of filter paper. If the transluscent spot appears on the paper, it confirms the presence of oil in groundnuts.

(*ii*) Now apply the other tests listed in Section 10.3.1 and record as suggested below :

Observations :

Experiment	*Observation*	*Inference*
1. Solubility in water of the extract.	Insoluble	Exrract is oil.
2. Perform acrolein test with extract.	Irritating smell.	Extract is oil.

Result. Groundnuts contain oil.

Experiment 10.4. To prove the presence of protein in egg white.

Apparatus. China dish, scissors, and other things as suggested in Experiment 10.1.

Materials. Eggs, distilled water, testing reagents (Section 10.3.2).

Procedure. Break a fresh egg in a china dish. Transfer the white of egg to a beaker. Release the protein from the membranes by cutting them repeatedly with scissors. Separate the egg white. Now take 5 mL of this egg white in a 100 mL measuring flask. Now make up the volume up to the mark by adding distilled water. Shake the contents until foam appears.

Now use this solution for carrying out the tests for protein listed in Section 10.4.2 and record the observations as suggested in earlier experiments.

Result. The egg white contains protein.

Note. Gelatin dispersion is prepared by adding gelatin (5g) to warm water (100 mL). Use the cold solution.

Experiment 10.5. To confirm the presence of carbohydrates, fats and proteins in the various samples of food.

(*i*) milk, (*ii*) apple juice, (*iii*) cashewnuts, etc.

Hint. 1. Tests for the presence of carbohydrate (lactose) and protein in milk. Heat the milk, say 100 mL, in a container until a semi-solid mass is obtained. Perform the various tests listed in Sections 10.2.1 and 10.4.2 using this semi-solid mass.

2. Test the presence of carbohydrate in apple juice. Perform the tests discussed in Section 10·2·1.

3. Test the presence of oil in the extract of cashewnuts. Perform the tests discussed in Section 10.3.1.

ORAL QUESTIONS AND ANSWERS

Q. 10.1. Name the various constituents of food ?

Ans. There are five vital constituents of food, viz. (*i*) carbohydrates, (*ii*) fats and oils (*iii*) proteins (*iv*) mineral salts, and (*v*) vitamins.

Q. 10.2. Give the difference between oils and fats.

Ans. Both oils and fats are esters of glycerol. The basic difference between oils and fats is that oils are liquids at room temperature whereas fats are solids. Also, oils have more unsaturation than fats.

Q. 10.3. What are the basic functions of carbohydrates, proteins and fats and oils in the body.

Ans. Carbohydrates are mainly required for the supply of energy to body. At times when carbohydrates are not in sufficient supply, fats and oils supply energy to the body. Proteins are exclusively required for building up tissues. They help in the regeneration of cells also.

Also refer to Sections 10.2, 10.3 and 10.4.

Q. 10.4. What is the general formula of carbohydrates ?

Ans. $C_n(H_2O)_m$.

Q. 10.5. What is the chemical nature of carbohydrates, proteins and fats ?

Ans. Refer to Sections 10.2, 10.3 and 10.4.

Q. 10.6. What is Fehling's solution ?

Ans. It is obtained by mixing two solutions say A and B. Solution A contains copper sulphate solution whereas the solution B contains potassium hydroxide and potassium sodium tartrate (also known as Rochelle salt).

Q. 10.7. Is Fehling's test given by all sugars ?

Ans. Fehling's test is given only by reducing sugars such as glucose, fructose, *etc*. but not by non-reducing like sucrose, starch, *etc.*

Q. 10.8. How would you test carbohydrate in apple juice ?

Ans. Take ~ 2 mL apple juice in a test tube. Add 1 mL of Molisch's reagent (alchoholic solution of α-naphthol) and a few drops of concentrated sulphuric acid by the side of the test tube. Appearance of a pink purple or violet colour at the junction of two layers shows the presence of carbohydrate in the apple juice.

Q. 10.9. What is the cause of violet colour in the Molisch's test ?

Ans. In the presence of conc. sulphuric acid carbohydrate gives furfural or one of its derivatives. These give a purple coloured product on coupling with α-naphthol.

Q. 10.10. What is Huble's solution ?

Ans. It is obtained by mixing equal volumes of 5% iodine solution in alcohol and 6% solution of mercuric chloride in alcohol. It is used for determining relative unsaturation in oils and fats.

Q. 10.11. What is Baudouin's test ?

Ans. It is helpful for detecting seasame oil present in vanaspati ghee.

Desi ghee does not contain such an oil. This test is helpful in differentiating two types of ghee.

Q. 10.12. (*i*) What are proteins ?

(*ii*) What is a peptide linkage ?

(*iii*) What is the role of amino acids in proteins.

Ans. Refer to Section 10.4.

Q. 10.13. What is a Millon's reagent ?

Ans. It is a solution of mercuric nitrate in nitric acid. It serves to identify proteins which contain the phenolic amino acid, *e g*. tyrosine.

Q. 10.14. What is Xanthoproteic test ?

Ans. It identifies the presence of amino acids which contain benzene ring. In this test, protein is heated with conc. HNO_3 when it becomes yellow.

Q. 10.15. Which are more unsaturated : oils or fats ?

Ans. Oils.

Q. 10.16. Describe the ninhydrin test. Give its chemistry.

Ans. Refer to Section 10.4.1.

□ □

UNIT 11

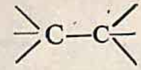
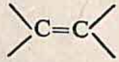
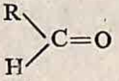
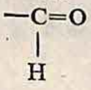
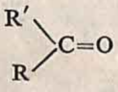
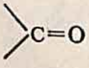
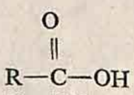
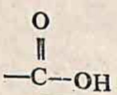
Identification of Functional Groups

11.1. INTRODUCTION

The large family of organic compounds containing only the elements carbon and hydrogen is appropriately named the hydrocarbons. Hydrocarbons are of importance because they may be considered as the basis of all the organic compounds. Replacement of hydrogen atom in a hydrocarbon by an —OH group gives an alcohol; a —COOH group gives a carboxylic acid. It is the presence of groups such as these in the molecules that produces the dominant chemical characteristics of substances. A substance is what it is—that is, it behavas as it does chemically—because of the presence of one or more functional groups. Thus, all organic compounds can be looked on as being derived from the hydrocarbons.

All compounds with the same functional group will undergo similar reactions. For example, the following alcohols : CH_3-OH, CH_3-CH_2-OH, $CH_3-CH(OH)-CH_3$, *etc.* The double and triple bonds of alkenes and alkynes are chemically reactive and are, thus, considered functional groups. The —C—C— bond is quite stable. Some of the common functional groups are given in the Table 11·1.

TABLE 11.1

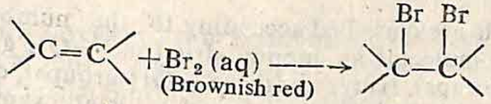
Name	*General structure formula*	*Functional group*
1. Alkane	$C_n H_{2n+2}$	
2. Alkene	C_nH_{2n}	
3. Alkyne	C_nH_{2n-2}	$-C\equiv C-$
4. Alcohol	$R-OH$	$-OH$
5. Aldehydes		 $\underset{\mid \atop H}{-C}=O$
6. Ketones		
7. Carboxylic acids	 $R-\overset{O \atop \parallel}{C}-OH$	 $-\overset{O \atop \parallel}{C}-OH$
8. Amines	$R-NH_2$	$-NH_2$
9. Nitro compounds	$R-NO_2$	$-NO_2$
10. Phenols	$Ar-OH$	$-OH$

In this unit, we will learn about the tests employed for the detection of unsaturation, alcoholic group, phenolic group, carboxylic acid group, ketonic group and amino group in an organic compound.

11.2. TESTS FOR UNSATURATION IN ORGANIC COMPOUNDS

Unsaturation in an organic compound is exhibited by $>C=C<$ and $-C\equiv C-$bonds present in the compound. Since such compouns react with bromine water to give addition compounds, bromine water can be used as to detect the unsaturation. Unsaturated compounds also react with alkaline potassium permanganate (Baeyer's reagent) giving characteristic oxidized products. Hence, Baeyer's reagent can be used for detecting unsaturation.

(*i*) **Bromine reagent test**. Dissolve a small quantity of the compound ($\sim$0.2 g or 0.2 mL) in about 1-2 mL of distilled water contained in a test tube. Add 1 mL bromine water solution drop by drop. Note the change in colour. If the colour of bromine disappears, the compound is considered to be unsaturated.



$$>C=C< + \underset{\text{(Brownish red)}}{Br_2(aq)} \longrightarrow >\overset{Br}{\overset{|}{C}}-\overset{Br}{\overset{|}{C}}<$$

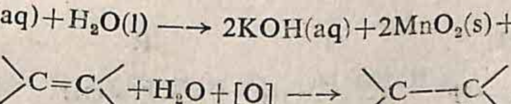
(Colourless)

Note. (*i*) If the organic compound is not soluble in water, a dilute solution of bromine in carbon tetrachloride is employed.

(*ii*) A gaseous organic compound is tested for its unsaturation by passing it through 1-2 mL of bromine solution. At times the compound can be tested by pouring 1 mL of bromine solution into the gas jar containing the compound (gas). Decolourization of brown-red colour of bromine shows unsaturation.

(*ii*) **Baeyer's test**. Take about 0.2 g (0.5 mL) of the compound in a test tube. Dissolve in 2 mL water in acetone. Now add 4-5 drops of 2% cold solution of alkaline potassium permananate in water (Na_2CO_3 is used to make the solution alkaline). Note the change in colour. If the purple colour disappears, the unsaturation in the compound is indicated. A brown ppt of MnO_2 is seen at the bottom of the test tube.

$$2\,KMnO_4\,(aq)+H_2O(l) \longrightarrow 2KOH(aq)+2MnO_2(s)+3[O]$$



$$>C=C< + H_2O+[O] \longrightarrow >\underset{OH}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}<$$

Note. The slightly alkaline or neutral aqueous solution of $KMnO_4$ is called Baeyer's reagent. Baeyer's test is sometimes called **hydroxylation** as it involves the addition of —OH group in a unsaturated compound. In case the reaction is carried out at high temperature the cleavage of the bond takes place. The colour of $KMnO_4$ solution can be discharged by certain reducing agents or groups like —OH, —CHO, *etc.* Hence, the test is not very reliable for unsaturation.

Precautions. (*i*) Handle the organic compounds carefully. (*ii*) Keep them away from the flame. (*iii*) Don't heat them directly over a flame. (*iv*) While performing the bromine solution test use the same solvent both for bromine and the compound. (*v*) Bromine is a corrosive liquid.

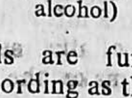
11.3. ALCOHOLS

The genenal formula for the monohydric alcohols is $C_nH_{2n+1}OH$ (or RHO). They may be regarded as alkane derivatives in which hydrogen is replaced by the hydroxyl group. RH, the alkane becomes ROH, the alcohol, where R is any alkyl group or benzyl group, for example, ethyl alcohol C_2H_5OH, benzyl alcohol $C_6H_5CH_2OH$, *etc.*

Alcohols are classified according to the number of hydroxyl groups in the molecule as monohydric (one —OH group), dihydric (two —OH groups), trihydric (three —OH groups), etc. Glycol is an example of dihydric alcohols and glycerol is an example of trihydric alcohols. When four or more hydroxyl groups are attached, they are called polyhydric alcohols.

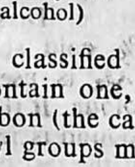
C_2H_5-OH

Ethanol
(A monohydric
alcohol)



$$\begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array}$$

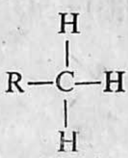
Glycol
(A dihydric
alcohol)



$$\begin{array}{l}CH_2-OH\\ |\\ CH-OH\\ |\\ CH_2-OH\end{array}$$

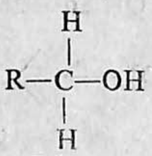
Glycerol
(A trihydric
alcohol)

Monohydric alcohols are further classified as primary, secondary and tertiary according as they contain one, two, or three alkyl groups attached to the alcohol carbon (the carbon to which hydroxyl group is attached). These alkyl groups may be same or different.



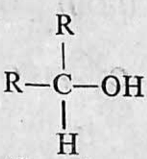
$$\begin{array}{c}H\\ |\\ R-C-H\\ |\\ H\end{array}$$

(An alkane)



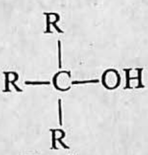
$$\begin{array}{c}H\\ |\\ R-C-OH\\ |\\ H\end{array}$$

(Primary
alcohol)



$$\begin{array}{c}R\\ |\\ R-C-OH\\ |\\ H\end{array}$$

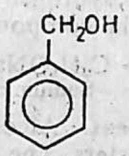
(Secondary
alcohol)



$$\begin{array}{c}R\\ |\\ R-C-OH\\ |\\ R\end{array}$$

(Tertiary
alcohol)

An aromatic alcohol is an aromatic compound that contains the hydroxyl group attached to a side chain :



Benzylalcohol
(Aromatic alcohol)

Its properties are more like that of an alcohol than a phenol. A phenol is an aromatic compound containing hydroxyl group attached to an aromatic ring.

11.3.1. THE —OH GROUP IN ALCOHOLS

In the —OH group in alcohol, the oxygen has six electrons, two of them unpaired, in its outer shell. **In the alcohols, one of the unpaired electrons of oxygen is bonded covalently to a carbon atom, the other to hydrogen** $:\!-\!\overset{|}{\underset{|}{C}}\times\overset{\cdot\cdot}{\underset{\cdot\cdot}{\dot{O}}}\times H$. The introduction of the highly electronegative oxygen atom significantly changes the properties of the hydrocarbons. The molecules become polar, as charge centres develop in the neighbourhood of oxygen.

$$\overset{\frac{1}{2}\delta+}{H_3C}-\overset{\delta-}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}}-\overset{\frac{1}{2}\delta+}{H}$$

All hydroxyl groups show acidic properties to a certain degree. They are acidic by virtue of the fact that hydrogen atom of the —OH group can be removed as H^+ by bases. The skeleton to which the group is attached, however, will iufluence the 'ease' with which protons can be removed. The acid character decreases as we move from a primary to secondary to tertiary alcohol because of increasing number of alkyl groups. Because the oxygen atom of the hydroxyl groups has lone pair of electrons, it is in principle possible for it to accept a proton from a stronger atom—in other words to behave as a base.

$$-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-H+H^+\longrightarrow -\underset{\cdot\cdot}{\overset{\overset{H}{|}}{O^+}}-H$$

11.3.2. TESTS FOR ALCOHOLIC—OH GROUP

(*i*) **Sodium metal test.** Take 2-3 mL of the compound in a dry test tube. Now add a small amount of anhydrous calcium chloride (dehydrating agent) to remove moisture. After sometime decant off the liquid compound to another dry test tube. To this add a freshly cut small piece of sodium metal. Brisk effervescence with evolution of hydrogen gas shows the presence of alcoholic functional group in the compound.

$$C_2H_5OH\ (l) + Na\ (s) \longrightarrow \underset{\text{Sodium ethanoate}}{C_2H_5ONa} + \tfrac{1}{2}H_2\ (g)$$

(*ii*) **Ester formation test.** Alcohols react with carboxylic acids forming sweat smelling esters. The reaction is called esterification. Take a 1-2 mL of the organic compound in a dry test tube. Add a few drops of glacial acetic acid and also that of concentrated sulphuric acid (works as a catalyst) to it. Warm the contents in a water bath for 5-10 min with occasional shaking. Smell the vapours coming out of the test tube. A characteristic pleasant smell due to the formation of ester shows the presence of alcohol.

$$\underset{\text{Ethanol}}{C_2H_5OH} + \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[H+]{H_2SO_4} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{water}}{H_2O}$$

(*iii*) **Ceric ammonium nitrate test.** Treat a few drops of the alcohol with ~ 1 mL of the ceric ammonium nitrate reagent. Appearance of red colour shows the possibility of alcoholic hydroxyl group.

$$2\ R{-}OH + \underset{\text{Ceric ammonium nitrate}}{(NH_4)_2\ Ce\ (NO_3)_6} \longrightarrow \underset{\text{(Red)}}{(ROH)_2\ Ce\ (NO_3)_4} + 2NH_4NO_3$$

(*iv*) **Xanthate test :** Take 1 mL of the compound in a test tube and about 1 g of powdered KOH. Warm the contents. Now cool the contents and add 4-5 drops of ether and CS_2. Shake the contents. Formation of yellow ppt. shows alcoholic —OH group.

(*v*) Iodoform test (Refer to Section 11.5.4).

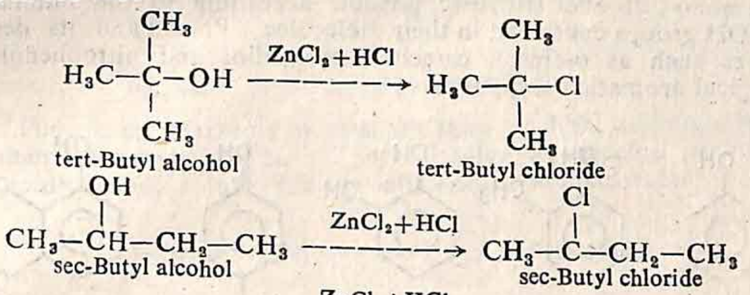
Precautions. (*i*) The alcohol should not contain water as it reacts with sodium metal to produce hydrogen gas.

(*ii*) Do not throw unreacted sodium metal into the sink or waste bin as it may cause fire. Add more alcohol to the unreacted sodium to complete the reaction.

11.3.3. Methods of Distinguishing Alcohols

(*i*) **Lucas test :** This test is based on the difference in reactivity of the three classes of alcohols towards the Lucas reagent (a mixture of concentrated hydrochloric acid and anhydrous zinc chloride). The reagent reacts with alcohols to form the corresponding insoluble alkyl chlorides with different speeds. Tertiary alcohols react immediately to give a cloudiness due to the formation of the chloride. With secondary alcohols, the cloudiness appears after a few minutes while with primary alcohols no appreciable reaction is observed at room temperature.

Take 1-2 mL of dry alcohol in a dry test tube and add 5-10 drops of Lucas reagent. Shake the reaction mixture well and warm the contents in a boiling water both. Observe the changes taking place in the tube.



$$\underset{\text{tert-Butyl alcohol}}{H_3C-\overset{\overset{\Large CH_3}{|}}{\underset{\underset{\Large CH_3}{|}}{C}}-OH} \xrightarrow{ZnCl_2+HCl} \underset{\text{tert-Butyl chloride}}{H_3C-\overset{\overset{\Large CH_3}{|}}{\underset{\underset{\Large CH_3}{|}}{C}}-Cl}$$

$$\underset{\text{sec-Butyl alcohol}}{CH_3-\overset{\overset{\Large OH}{|}}{C}H-CH_2-CH_3} \xrightarrow{ZnCl_2+HCl} \underset{\text{sec-Butyl chloride}}{CH_3-\overset{\overset{\Large Cl}{|}}{C}-CH_2-CH_3}$$

$$CH_3-CH_2-OH \xrightarrow{ZnCl_2+HCl} \text{No reaction.}$$

(*ii*) **Oxidation with $K_2Cr_2O_7$ or $KMnO_4$:** Primary alcohols are first oxidized to aldehydes and then to carboxylic acids containing the same number of carbon atoms, as the original alcohols.

Secondary alcohols are oxidized to ketones, with the same number of carbon atoms, as the original alcohols. The ketone on further drastic oxidation gives an acid with a lesser number of carbon atoms than the original alcohol.

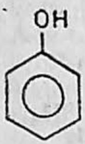
Teritary alcohols do not undergo any oxidation in neutral or alkaline medium. With acid oxidizing agents, they give a mixture of ketones and carboxylic acids each containing a lesser number of carbon atoms than the original alcohol.

Table 11 2 Methods of distinguishing between primary, secondary and tertiary alcohols

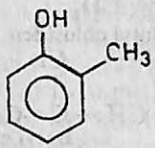
Reagent	*Primary alcohol*	*Secondary alcohol*	*Tertiary alcohol*
Acidified $K_2Cr_2O_7$ (orange)	Aldehyde, RCHO formed [blue Cr^{3+} (aq) formed]	Ketone, R_2CO formed [blue Cr^{3+} (aq) formed]	Resists oxidation
Conc. H_2SO_4	Alkene formed slowly	Intermediate in speed	Alkene formed fast
Lucas reagent (Conc. HCl $+ZnCl_2$) Add to alcohol and place in boiling water bath.	Cloudiness due to formation of RCl is slow to appear. (Anhydrous conditions are needed for primary alcohols.)	Cloudiness appears in 5 minutes due to the formation of RCl	Cloudiness appears in 1 minute owing to the formation of RCl, which is insoluble in water.

11.4. PHENOLS

Phenols are aromatic compounds in which —OH group is substituted directly on the benzene ring. The compounds are classified as mono-, di- and trihydric phenols according to the number of —OH groups contained in their molecules. Phenol and its derivatives such as o-cresol, catechol, pyrogallol and nitrophenol are typical aromatic compounds.

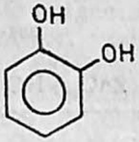


Phenol

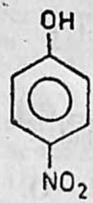


o-Cresol

(Monohydric)

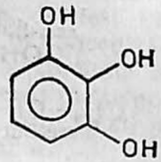


Catechol



p-Nitrophenol

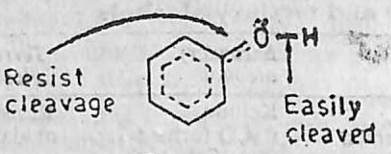
(Dihydric)



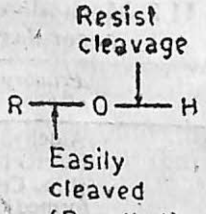
Pyrogallol
(Trihydric)

11.4.1. The —OH Group in Phenol

A lone pair of electrons associated with the oxygen of phenolic —OH interacts with the π-system of the benzene ring and is delocalized over the entire molecule. As a result of delocalization of electrons, the —C—O— bond acquires some double character and becomes stronger than —O—H σ-bond. Also the increased electron density in the benzene ring activates it, and gives electrophillic substitution reactious.



Phenol
(Resonance hybrid)

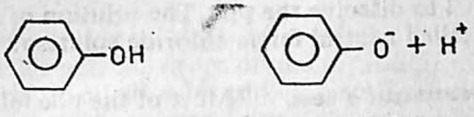


(R = alkyl)

In alcohols, no resonance is thus possible. The non-bonded electrons remain localized on the oxygen atom. The $\overset{\sigma}{—C—}OH$ linkage retains its σ bond character and is weak as compared to that in phenols.

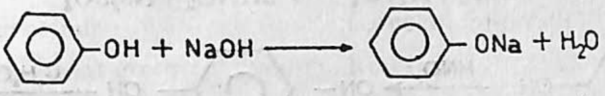
11.4.2. Tests for Phenol (—OH) Group

(*i*) **Acid character :** Phenols behave as weak acids because they ionize when dissolved in water to form phenoxide ion.



Phenol Phenoxide ion

Phenols are markedly more acidic than alcohols, although less so than carboxylic acids. They dissolve in aqueous sodium hydroxide to form soluble sodium salts known as phenoxide.



Phenol Sodium phenoxide

The introduction of nitro (—NO_2) and chloro groups increases the acidity of the phenols.

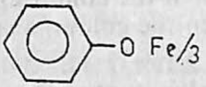
Acidity of phenol is due to two reasons :

—Resonance stabilisation of benzene ring by the non-bonded electron pair present on oxygen atom of the phenolic —OH.

—Resonance stabilisation of phenoxide ion.

The acidic nature can be confirmed by litmus test. If the litmus solution or paper turns red then phenol may be present. No effervescence is seen with sodium hydrogen carbonate.

(*ii*) **Tests with $FeCl_3$ solution** : Phenols form coloured iron complexes with neutral $FeCl_3$. This reaction is often used as a test for phenols. Phenol gives violet colouration.



Iron complex

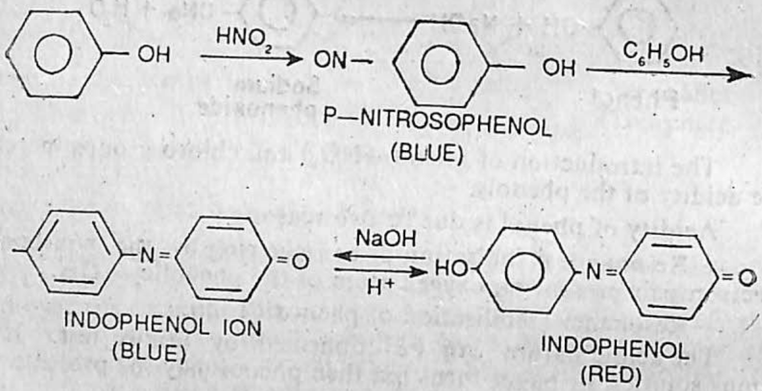
To 1-2 mL of the aqueous or alcoholic solution of the compound contained in a test tube add a few drops of neutral ferric chloride solution. Appearance of green, blue or violet colour shows the presence of phenolic group.

Violet	—phenol, o-cresol, salicylic acid
Green	—catechol
Blue changing to red	—pyrogallol, hydroquinone
Green colour in alcoholic solution	—o-, -m-, -p- cresols, resorcinol β-naphthol
Bluish violet colour in alcoholic solution	—α-naphthol

Note : To prepare neutral ferric chloride take 1 mL of the acidic solution of ferric chloride solution in a test tube. Add aqueous ammonia drop by drop until you get brownish ppt. Now add 1-2 drops of dil. HCl to dissolve the ppt. The solution of ferric chloride so produced is called neutral ferric chloride solution.

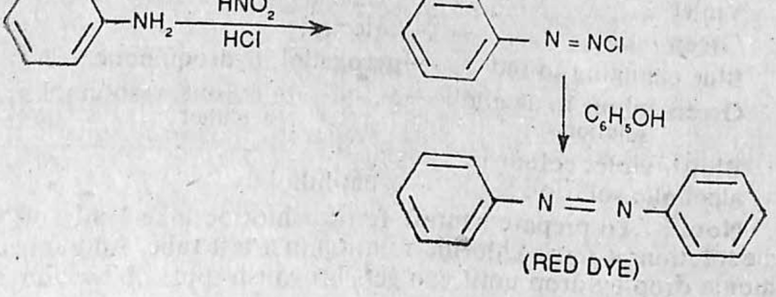
(*iii*) **Liebermann's test** : Most of the phenols produce red or brown coloured product when $NaNO_2$ is added to a solution of the phenol in conc. H_2SO_4. The colour changes to red when an excess of water is added. The solution agains turns blue or green on adding caustic soda.

$$2NaNO_2 + H_2SO_4 \longrightarrow 2HNO_2 + Na_2SO_4$$



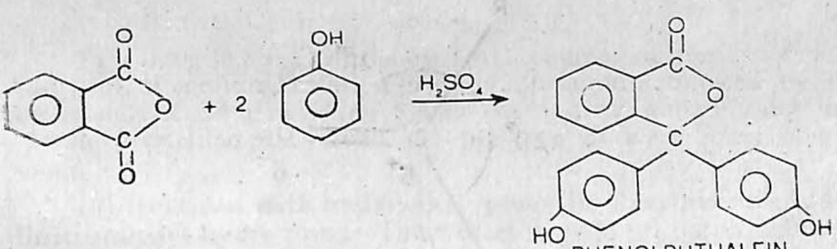
Take a compound (~0.5 g) in a test tube. Add a few crystals of $NaNO_2$ and 1 mL of conc. H_2SO_4. A green or blue colour is developed on warming the contents in a water-bath. Pour the contents into water, when the colour changes to red. Now add excess of caustic soda, when the colour again changes to green or blue.

(*iv*) **Azo-dye formation test :** Treat 1-2 drops of aniline in a test tube with 0.5–1 mL of conc. HCl. Dilute contents with water, cool in a freezing mixture bath and add aqueous solution of $NaNO_2$ with stirring. Mix this diazotized solution with alkaline solution of (~2N NaOH) phenol. Appearance of orange or red colour due to dye formation shows the presence of phenolic —OH group.



(*v*) **Phthalein test :** Heat 0.5 g of the compound with 1 g phthalic anhydride and 2-3 drops of conc. H_2SO_4. Cool and make the reaction mixture alkaline by adding NaOH solution. Pour a few drops of the alkaline reaction solution into ~20 mL of water. Appearance of red colour or yellow green fluorescence indicates the presence of phenolic —OH group.

Red colour	—	Phenol, o-cresol
Blue colour	—	Catechol, m-cresol
Fluorescent green	—	Resorcinol
No colour	—	p-cresol



PHENOLPHTHALEIN
(IN ACIDIC MEDIUM)

Precautions. Phenols are corrosive compounds. Handle them carefully. Don't touch them or let them fall on your skin.

11.5. ALDEHYDES AND KETONES

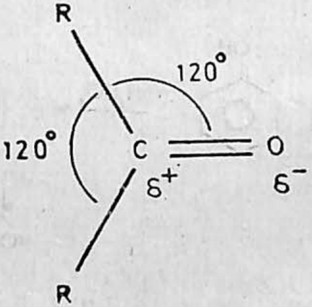
Aldehydes and ketones are the first oxidation products of primary and secondary alcohols respectively. They constitute two isomeric series of carbon compounds, with the general formula $R—\overset{\overset{O}{\|}}{C}—H$ for aldehydes and $R—\overset{\overset{O}{\|}}{C}—R'$ for ketones. Here R and R' could be alkyl or aryl groups and they could be same or different. The $\rangle C=O$ group is the functional group and is called carbonyl group. The single hydrogen atom attached to this group also displays a special reactivity and is responsible for the differences between the chemical properties of aldehydes and ketones.

Formaldehyde is the smallest molecule in which the $\rangle C=O$ group is attached to two hydrogen atoms (one hydrogen is in place of R and the other is a part of aldehydic group).

11.5.1. Nature of the Carbonyl Group

The carbonyl group has a geometry similar to that of the carbon-carbon double bond in alkenes.

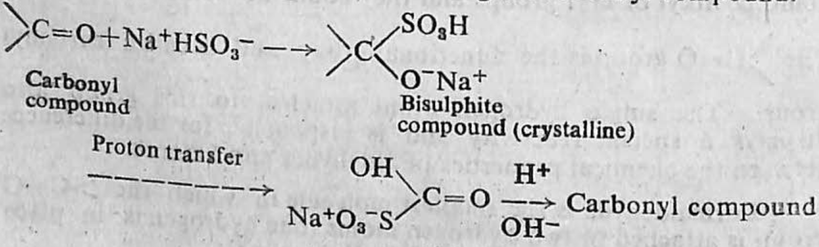
The carbonyl group has a double bond between carbon and oxygen and because of a difference in electronegativity between these two, the π-electrons are not equally shared. Oxygen being more electronegative, the electron cloud is polarized towards the oxygen, which pulls the mobile π-electrons to itself. This polarization of electrons results in a high dipole moment (2.3 to 2.8 D) for carbonyl compounds. The $\rangle C{=}O$ double bond thus differs from $-C{=}C-$ bond of alkenes which is non-polar in nature.



The carbon atom of $\rangle C{=}O$ is sp^2 hybridized and is joined to three bonds which lie in a plane making an angle of 120° with one another.

11.5.2. Tests for Aldehydes (—CHO) and Ketones (RCOR′)

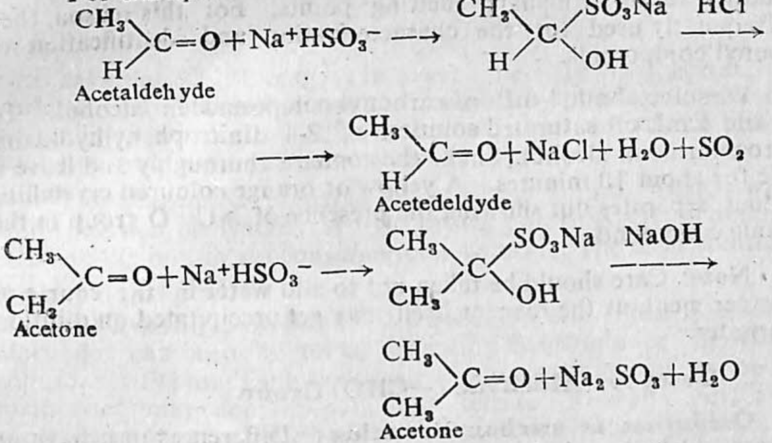
(*i*) **Addition of sodium hydrogen sulphite** : Aldehydes and ketones react with sodium hydrogen sulphite (sodium bisulphite) forming addition compounds. The addition product on treatment with acids or alkalis regenerate the original carbonyl compound.



$$\rangle C{=}O + Na^+HSO_3^- \longrightarrow \rangle C\begin{smallmatrix} SO_3H \\ O^-Na^+ \end{smallmatrix}$$

$$\xrightarrow{\text{Proton transfer}} \begin{smallmatrix} OH \\ Na^+O_3^-S \end{smallmatrix}\rangle C{=}O \underset{OH^-}{\overset{H^+}{\longrightarrow}} \text{Carbonyl compound}$$

For example :



$$\underset{\text{Acetaldehyde}}{CH_3(H)C=O} + Na^+HSO_3^- \longrightarrow CH_3(H)C(SO_3Na)(OH) \xrightarrow{HCl} \underset{\text{Acetedeldyde}}{CH_3(H)C=O} + NaCl + H_2O + SO_2$$

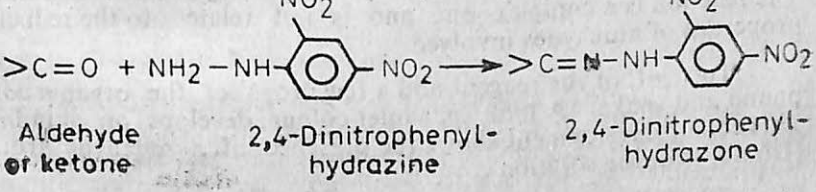
$$\underset{\text{Acetone}}{(CH_3)_2C=O} + Na^+HSO_3^- \longrightarrow (CH_3)_2C(SO_3Na)(OH) \xrightarrow{NaOH} \underset{\text{Acetone}}{(CH_3)_2C=O} + Na_2SO_3 + H_2O$$

Take 0.2 g (0.5 mL) of the carbonyl compound in a test tube. Add 1 mL of saturated solution of sodium bisulphite followed by a few crystals of sodium acetate. Shake the contents well. Formation of white crystalline ppt. shows the presence of a carbonyl compound.

(*ii*) **Reaction with hydrazine, phenylhydrazine and 2, 4-dinitrophenyl hydrazine** : These react to yield the corresponding condensation hydrazones.

$$\underset{\text{Aldehyde or ketone}}{>C=O} + \underset{\text{Hydrazine}}{NH_2-NH_2} \longrightarrow \underset{\text{Hydrazone}}{>C=N-NH_2} + H_2O$$

$$\underset{\text{Aldehyde or ketone}}{>C=O} + \underset{\text{Phenylhydrazine}}{NH_2-NH-C_6H_5} \longrightarrow \underset{\text{Phenylhydrazone}}{>C=N-NH-C_6H_5} + H_2O$$



Aldehyde or ketone 2,4-Dinitrophenylhydrazine 2,4-Dinitrophenylhydrazone

The reagents if used as free amines are easily oxidizable by air and, therefore, are usually employed as their salts, *e.g.* hydroxyl amine hydrochloride, $NH_2OH.HCl$; phenylhydrazine hydrochloride, $C_6H_5-NH-NH_2.HCl$, *etc.* The products of reaction are mostly crystalline solids with sharp melting points. For this reason, they are frequently used for the characterization and identification of carbonyl compounds.

Dissolve about 1 mL of carbonyl compound in alcohol. To this add 1 mL of saturated solution of 2-4 dinitrophenylhydrazine hydrochloride in alcohol. Shake the contents thoroughly and leave it aside for about 10 minutes. A yellow or orange coloured crystalline product separates out showing the presence of $>C{=}O$ group in the organic compound.

Note: Care should be taken not to add water in the course of the experiment, as the reagent itself may get precipitated on dilution with water.

11.5.3. Tests for Aldehyde (—CHO) Group

Oxidation to carboxylic acids : Differences in behaviour between aldehydes and ketones towards oxidizing agents constitute the main difference between aldehydes and ketones. This is because aldehydes are easily oxidizable by mild oxidizing agents like Tollen's reagent, Fehling's and Benedict's solutions and Schiff's reagent to carboxylic acids containing the same number of carbon atoms whereas ketones can be oxidized only under drastic conditions when they yield lower acids. Oxidation of ketone requires the cleavage of C—C bond.

$$RCHO \xrightarrow[\text{Mild conditions}]{[O]} RCOOH$$

$$RCH_2{-}CO{-}R \xrightarrow[\text{Drastic conditions}]{[O]} 2\,RCOOH$$

(*i*) **Schiff's reagent test** : Aldehydes react with **Schiff's reagent** producing a characteristic colour. This reagent is a solution of a magenta dye (rosaniline hydrochloride) which has been decolourized by passing sulphur dioxide through the water solution. Aldehydes on reacting with reagent rapidly restore colour. The reaction is a complex one and is not related to the reducing properties of aldehydes involved.

To 1 mL of the reagent add a few drops of the organic compound and shake. A pink or violet colour develops on standing. This colour development shows the presence of a aldehyde group. (Do not heat the solution).

(*ii*) **Tollen's reagent test** : The presence of aldehydes can be tested by **Tollen's reagent** (ammoniacal silver nitrate solution). The diammine silver (I), ion $[Ag(NH_3)_2]^+$ is reduced to metallic silver on warming with aldehyde. The silver mirror deposits on the walls of the container.

$$RCHO + 2[Ag(NH_3)_2]OH \longrightarrow RCOOH + \underset{\text{(Silver mirror)}}{2Ag} + H_2O + 4NH_3$$

Take the 2-3 mL reagent in a test tube. To this add 0.5 g or 1 mL of the compound. Warm the contents by placing the test tube in a boiling water bath. Appearance of silver mirror or greyish black ppt. shows the presence of aldehyde group.

The reagent is prepared by treating 1-2 mL $AgNO_3$ with a dilute solution of NaOH. A light brown ppt. of AgOH is obtained. Dissolve the ppt. in aqueous ammonia solution. The clear solution is called Tollen's reagent.

(*ii*) **Fehling's or Benedict's solution test** : The presencc of aldehydes can also by tested by using **Fehling's** or **Benedict's** solutions. Fehling's solution is an alkaline solution of copper sulphate containing sodium potassium tetrate (Rochelle salt) as the complexing agent. Benedict's solution is an alkaline solution of copper sulphate containing sodium citrate as complexing agent.

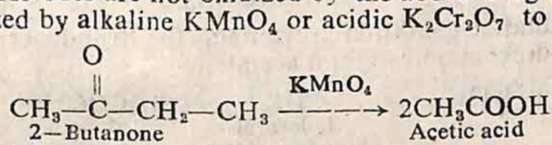
Aliphatic aldehydes on warming with Fehling's or Benedict's solution give a brick red precipitate of cuprous oxide on reduction of the alkaline Cu(II).

$$CH_3CHO + Cu(OH)_2 \longrightarrow \underset{\text{(Red precipitate)}}{Cu_2O} + H_2O + CH_3COOH$$

The blue colour of the Fehling's solution changes to green, yellowish and finally brick red due to the formation of red ppt. of Cu_2O.

Take 2 mL of aqueous solution of the aldehyde and add 1 mL of the Fehling's solution. Warm the reaction mixture in a water bath for some time. Formation of red ppt. shows the presence of aldehyde.

Ketones are not oxidized by the above reagents. Ketones are oxidized by alkaline $KMnO_4$ or acidic $K_2Cr_2O_7$ to carboxylic acids.



$$\underset{\text{2-Butanone}}{CH_3-\overset{\overset{O}{\parallel}}{C}-CH_2-CH_3} \xrightarrow{KMnO_4} \underset{\text{Acetic acid}}{2CH_3COOH}$$

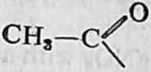
11.5.4. Tests for Ketones only

(*i*) **m-Dinitrobenzene test** : Take 4-5 drops (if liquid) or or 0.2 g (if solid) of the organic substance in a dry test tube. Add a pinch of powdered m-dinitrobenzene followed by 4-5 mL of NaOH solution and shake well. If a violet colour appears which fades on standing, confirms the presence of ketone.

Note : Benzophenone does not respond to this test.

(*ii*) **Sodium nitroprusside test** : Take 2 mL of a freshly prepared solution of sodium nitroprusside in a test tube. Add 2 mL of the aqueous solution of the compound followed by the addition of caustic soda solution drop by drop. If a wine red or red orange colour appears which changes to purple on addition of acetic acid, confirms the presence of a ketone.

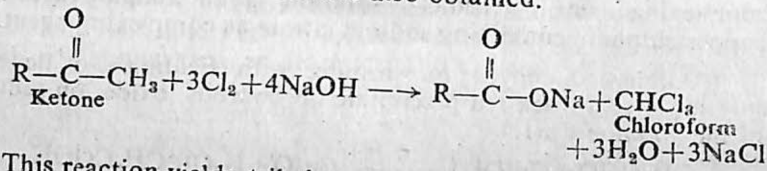
Note : This test is given by ketones (*e.g.* acetone) which contains



group.

(*iii*) Ketones are unable to restore the colour of the Schiff's reagent. Ketones are also unable to reduce ammonical silver nitrate (Tollen's reagent) or Fehling's solution.

(*iv*) **Haloform reaction**. A carbonyl compound containing at least one methyl group adjacent to $>C=O$ group on treating with a halogen in sodium hydroxide is oxidized to a carboxylic acid. A trihalogen methane derivative is also obtained.



$$\underset{\text{Ketone}}{R-\overset{\overset{O}{\|}}{C}-CH_3}+3Cl_2+4NaOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-ONa+\underset{\text{Chloroform}}{CHCl_3}+3H_2O+3NaCl$$

This reaction yields trihalomethanes—chloroform, bromoform and iodoform depending upon the halogen used. Since the common name for the compound is haloform, it is called haloform reaction.

Acetaldehyde is the only aldehyde which gives haloform reaction. This reaction serves as a test for the presence of CH_3CO-group. For this purpose reaction is carried out with iodine and alkali, when a yellow ppt of iodoform is obtained. This is known as iodoform test.

$$\underset{\text{Acetone}}{CH_3CO\,CH_3}+3I_2+3OH^- \longrightarrow \underset{\text{Triiodoacetone}}{CI_3\,CO\,CH_3}+3H_2O+3I^-$$

Under the alkaline condition prevailing, the triiodoacetone is broken up into iodoform and sodium acetate.

$$CI_3\,COCH_3+NaOH \longrightarrow \underset{\substack{\text{Iodoform}\\\text{(Triiodomethane)}}}{CHI_3}+\underset{\text{Sodium acetate}}{CH_3COONa}$$

With acetaldehyde :

$$CH_3CHO+3I_2+3OH^- \longrightarrow CI_3CHO+3H_2O+3I^-$$

$$\underset{\text{Triiodo acetaldehyde}}{CI_3CHO}+NaOH \longrightarrow \underset{\text{Iodoform}}{CI_3H}+\underset{\text{Sodium formate}}{HCOONa}$$

Note : Secondary methyl alcohols, and only ethanol of primary alcohols react with iodine in presence of sodium hydroxide to give yellow precipitate of iodoform.

$$\underset{\text{sec-Methyl alcohol}}{CH_3CH(OH)-R}+I_2+2NaOH \longrightarrow CH_3COR+2NaI+2H_2O$$

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 4I_2 + 6NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + HCOONa + 5NaI + 5H_2O$$

Take 0·5 mL of the given compound in a clean dry test-tube and add about 1 mL of 1% iodine solution. Then add dilute sodium hydroxide solution (5%) drop by drop until the brown colour of iodine is discharged. Warm gently in a water bath. Observe the formation of a precipitate. Formation of yellow precipitate of iodoform indicates ethanol, acetaldehyde, sec-methyl alcohol or methyl ketone.

11.5.5. Distinguishing Tests for Aldehydes and Ketones

Reagent/test	*Aldehyde*	*Ketone*
Tollen's reagent	Ag mirror	No Ag mirror
Fehling's solution	Red ppt.	No red ppt.
Schiff's reagent	Pink colour	No pink colour
Phenylhydrazine	Crystalline phenylhydrazone	Crystalline phenylhydrazone
m-Dinitrobenzene	—	Violet colour, fades on standing.

11.6. CARBOXYLIC ACIDS

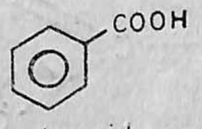
These compounds are characterized by the presence of the carboxyl groups $-\overset{\overset{O}{/\!/}}{C}-OH$. The term carboxyl is a combination of the terms, carbonyl ($-\overset{\overset{O}{\|}}{C}-$) group and hydroxyl (—OH), hence, the name carboxyl group. However, the properties of the carboxyl group are quite distinct from the properties of these two groups.

Compounds which contain one carboxyl attached to an alkyl or aryl group are called monocarboxylic acids. The carboxylic acids are classified as mono-, di-, tri... or polycarboxylic acids according to the number of carboxyl groups present in them.

The aliphatic monocarboxylic acids are also referred to as fatty acids, as some of the higher members ($C_{12}-C_{18}$) occur in natural fats as esters from which they are obtained by the hydrolysis.

According to the attachment of carboxyl group to alkyl or aryl group, the acids are known as aliphatic or aromatic carboxylic acids respectively.

CH_3CH_2COOH
Propanoic acid
(Aliphatic acid)



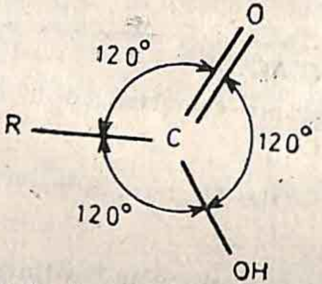
Benzoic acid
(Aromatic acid)

Hydrogen atoms of the alkyl or aryl group may be substituted by some other groups, such as —OH. —NH_2. —X, *etc*. Such acids are known as substituted carboxylic acid.

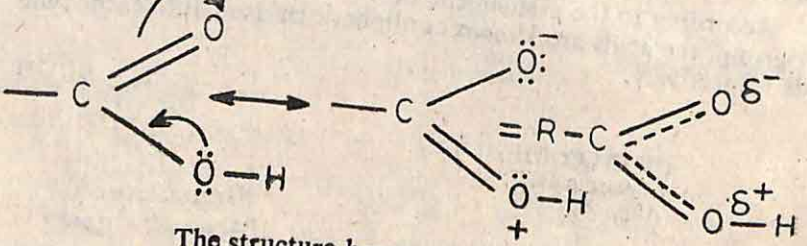
$X-CH_2COOH$	NH_2-CH_2COOH	$HO-CH_2-COOH$
(Halogen acid)	(Amino acid)	(Hydroxy acid)

11.6.1. Nature of the Carboxyl Group

The carbon atom of the $-\overset{\overset{O}{/\!/}}{C}-OH$ is sp^2 hybridized and is joined to three σ-bonds which including carbon lie in a plane making an angle of 120° with one another. These three σ-bonds are derived from the overlapping of three sp^2 hybridized orbitals of the carboxylic carbon with two sp^2 orbitals of two oxygen atoms and one sp^3 hybridized orbital of the alkyl group.



The >C=O group has a double bond between carbon and oxygen and because of difference in electronegativity between these two, the π-electrons are not equally shared. The electron cloud is polarized towards the oxygen. In this process, —OH bond is weakened as >C=O group tends to pull electrons on oxygen in $-\ddot{O}H$ towards itself. Hence the π electrons are partially delocalized between carbon and one oxygen on the one hand and the carbon and second oxygen on the other hand. Thus, the carboxyl is a resonance hybrid of the following two structures.



The structure has separated charges.

11.6.2. Tests for Carboxylic (—COOH) Group

(*i*) **Acidity**. Next to mineral acids, carboxylic acids are the most acidic amongst the organic compounds. In aqueous solution they furnish hydronium and carboxylate ions.

$$\underset{\text{Carboxylic acid}}{RCOOH} + H_2O \longrightarrow \underset{\text{Carboxylate ion}}{RCOO^-} + \underset{\text{Hydronium ion}}{H_3O^+}$$

These acids affect indicators, litmus solution and neutralize alkalis forming salts. They liberate carbon dioxide from carbonates, *etc*.

$$2CH_3COOH+Na_2CO_3 \rightarrow CO_2+H_2O+2CH_3COONa$$

$$\underset{\text{Acetic acid}}{CH_3COOH}+NaHCO_3 \rightarrow CO_2+H_2O+\underset{\text{Sodium acetate}}{CH_3COONa}$$

(*a*) **Litmus test**. Place a few drops of the organic compound (in liquid or aqueous solution) on a piece of moist blue litmus paper, or add to a blue litmus solution. If the colour changes to red, carboxylic group may be present.

Phenols also give this test.

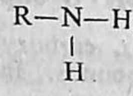
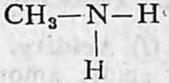
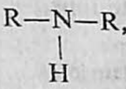
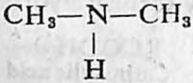
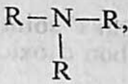
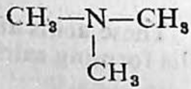
(*b*) **Sodium bicarbonate test.** Take ∼5 mL cold and dilute aqueous solution of sodium bicarbonate in a test tube. Now add a small amount of the organic compound if solid or a few drops if liquid. A strong effervescenee with the evolution of carbon dioxide gas shows the presence of carboxylic acid.

(*ii*) **Ester formation test.** Take a small amount of organic compound in a dry test tube. Add 5—10 drops of ethyl alcohol and 1—2 mL of conc. H_2SO_4. Heat the test tube in a boiling water bath. A pleasant fruity smell of ester shows the presence of carboxylic group.

$$\underset{\text{Acetic acid}}{CH_3COOH}+\underset{\text{Ethanol}}{C_2H_5OH} \overset{H+}{\rightleftharpoons} \underset{\text{Ethylacetate}}{CH_3COOC_2H_5}+H_2O$$

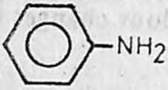
11.7. AMINES

The amines may be regarded as derivatives of ammonia, in which one or more hydrogen atoms have been replaced by alkyl or aryl groups. They are classified as primary, secondary or tertiary amines according as one, two or three hydrogen atoms of ammonia are substituted. The substituents in secondary and tertiary amines may or may not be the same. When all the alkyl groups are the same the amine is named as a simple or symmetrical amine and when two or all the three alkyl groups are different the amine is often called mixed or unsymmetrical amine. Thus :

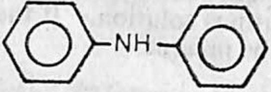
(*i*) Primary amines	 $\mathrm{R{-}\underset{\underset{\displaystyle H}{\vert}}{N}{-}H}$, *e.g.*	Methyl amine	 $\mathrm{CH_3{-}\underset{\underset{\displaystyle H}{\vert}}{N}{-}H}$
(*ii*) Secondary amines	 $\mathrm{R{-}\underset{\underset{\displaystyle H}{\vert}}{N}{-}R}$, *e.g.*	Dimethyl amine	 $\mathrm{CH_3{-}\underset{\underset{\displaystyle H}{\vert}}{N}{-}CH_3}$
(*iii*) Tertiary amines	 $\mathrm{R{-}\underset{\underset{\displaystyle R}{\vert}}{N}{-}R}$, *e.g.*	Trimethyl amine	 $\mathrm{CH_3{-}\underset{\underset{\displaystyle CH_3}{\vert}}{N}{-}CH_3}$

A fourth type of compound called quaternary ammonium salts are obtained by replacement of all the four hydrogen atoms of the ammonium cation by alkyl or aryl substituents, *e.g.*, $(CH_3)_4N^+I^-$, tetramethyl ammonium iodide.

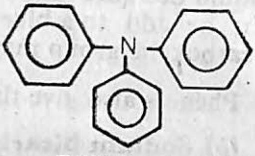
When one or more aryl groups are substituted in place of hydrogen into ammonia, the amine is called an aromatic amine.



Aniline
(Primary)



Diphenylamine
(Secondary)

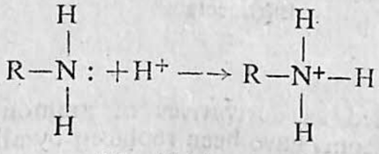


Triphenylamine
(Tertiary)

The functional group in three types of amines are, $-NH_2$ group (amino) $>$NH group (imino) and $\rightarrow$ N group (tertiary nitrogen atom).

11.7.1. Tests for Amino Group

(*i*) **Basic nature.** Like ammonia, all aliphatic amines are basic in nature. They owe their basic character to the lone pair of electrons on nitrogen and can form strong bonds to protons (Lewis concept).



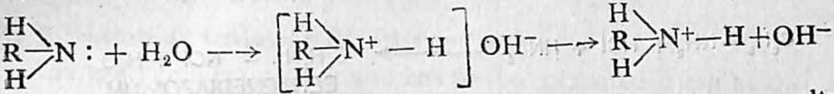
$$\mathrm{R{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{N}}{:} + H^{+} \longrightarrow R{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{N^{+}}}{-}H}$$

The ease with which the lone pair can bond to the proton, and hence the base strength of the compound, depends upon the groups attached to nitrogen. If the substituent group is electron withdrawing (—I), the base strength is reduced because of its lesser ability to form donor bond with the proton.

An alkyl group adjacent to nitrogen increases the availability of the electrons (+I effect), and so aminoalkanes are stronger bases than ammonia. In case of aryl amines, the basic character is less as the aryl group withdraws electrons from the nitrogen atom.

Typical reactions with water and acids are :

With water. Aliphatic amines dissolve in water forming quaternary ammonium hydroxides, which furnish hydroxyl ions on dissociation,



$$\mathrm{R{-}\overset{H}{\underset{H}{N}}: + H_2O \longrightarrow \left[R{-}\overset{H}{\underset{H}{N^+}}-H\right]OH^- \longrightarrow R{-}\overset{H}{\underset{H}{N^+}}-H + OH^-}$$

With acids. Amines react with acids forming quaternary salts, *e.g.*,

$$CH_3-NH_2+HCl \longrightarrow \underset{\text{(Methyl ammonium chloride)}}{CH_3N^+H_3Cl^-\ (CH_3NH_2.HCl)}$$

Thus even water insoluble amines like aniline are converted into water soluble salts.

$$C_6H_5NH_2 + HCl \longrightarrow C_6H_5N^+H_3Cl^-$$

All amines are weaker bases than NaOH and so are released from their salts by treating with aqueous alkali.

$$CH_3NH_3^+\,Cl^- + NaOH \longrightarrow CH_3NH_2+H_2O+NaCl$$

(*i*) **Litmus paper test** : Place a few drops of the organic compound if liquid (if solid, its aqueous solution) over a moist red litmus paper or add to a red litmus solution. If the red litmus paper turns blue, it indicates the presence of the amino group.

(*ii*) **Carbylamine test** : Take ~ 0.5 g (or 5-10 drops of the organic compound in a test tube. Now add 5-10 drops of chloroform and 2-5 mL of alcoholic solution of potassium hydroxide and warm in a boiling water bath. A highly offensive odour of isocyanide is obtained if the organic substance contains the primary amino group.

$$RNH_2+CHCl_3+3KOH \longrightarrow \underset{\text{Carbylamine}}{RNC}+KCl+3H_2O$$

Note : (*a*) Isocyanides are very poisonous. Destroy the compound by adding conc. HCl.

(*b*) Both aliphatic and aromatic amines give the test.

(*c*) Only primary amines gives this test.

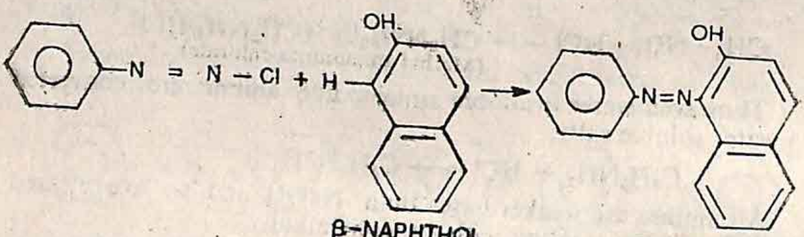
(*iii*) **Nitrous acid test** : Dissolve about 0.2 g of the organic compound in 5-10 mL dilute HCl and cool. Now add a few mL of 10% aqueous $NaNO_2$. A brisk effervescence shows the presence of aliphatic primary amine.

$$R-NH_2+HNO_2 \longrightarrow ROH + H_2O + N_2$$

HNO_2 behaves differently with sec or tert-amines.

(*iv*) **Azo-dye Test** : This test is given by aromatic primary amines only. Dissolve 0.5-1 g (or 5-10 drops) of the organic compound contained in a test tube in 1-2 mL of conc. HCl. Cool the reaction mixture in ice. Add 2-3 mL ice-cold 10% $NaNO_2$ solution and shake. Pour the reaction mixture into a beaker containing 5-10 mL of 10% alkaline β-naphthol. The formation of a red or orange dye confirms the presence of aromatic NH_2 group.

$$C_6H_5-NH_2 + HCl + HNO_2 \longrightarrow \underset{\text{BENZENEDIAZONIUM CHLORIDE}}{C_6H_5N = NCl} + H_2O$$



β-NAPHTHOL

PHENYL AZO β-NAPHTHOL (RED OR ORANGE DYE)

Tests to distinguish between primary, secondary and tertiary amines.

(*i*) **Hinsberg's test :** The amine is treated with benzene sulphonyl chloride, $C_6H_5SO_2Cl$ and excess of aqueous potassium or sodium hydroxide.

A primary amine yields a clear solution which on acidification yields an insoluble sulphonamide. This dissolves in potassium hydroxide, due to the formation of the potassium salt of the enolic sulphonamide.

$$RNH_2+C_6H_5SO_2Cl \xrightarrow{OH^-} [C_6H_5SO_2\underset{\underset{\text{Replaceable hydrogen}}{H}}{\underset{|}{N}}R] \xrightarrow[-H_2O]{KOH} \begin{array}{c}[C_6H_5SO_2NR]^- K^+ \\ \text{(Soluble)} \\ \Big\downarrow{\scriptstyle H^+ \text{ Acid}} \\ C_6H_5SO_2\,NH\,R \\ \text{(Insoluble)}\end{array}$$

A secondary amine yields an insoluble compound unaffected by acid (since it has no replaceable hydrogen):

$$R_2NH+C_6H_5-SO_2Cl \xrightarrow{KOH} \underset{\text{(Insoluble in KOH)}}{C_6H_5SO_2NR_2} \xrightarrow[H^+]{\text{NaOH or}} \text{No action}$$

The tertiary amine does not react with benzenesulphonyl chloride.

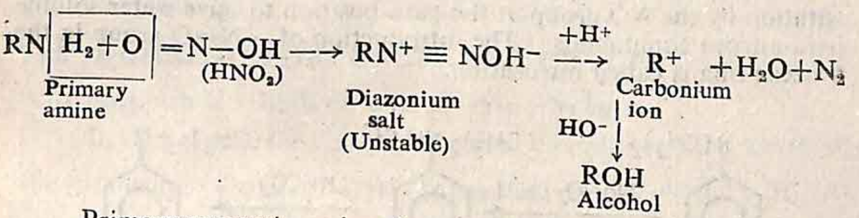
A tertiary amine yields an insoluble compound (the unchanged amine itself) which dissolves upon acidification of the mixture,

$$R_3N + C_6H_5SO_2Cl \xrightarrow{NaOH} \underset{(Insoluble)}{R_3N} \xrightarrow{HCl} \underset{(Soluble)}{R_3N^+HCl^-}$$

(*ii*) **Reaction of amines with nitrous acid**

Nitrous acid is unstable and has to be prepared fresh by dissolving sodium nitrite in dilute hydrochloric acid. Primary, secondary and tertiary amines behave differently. The reaction can thus be used for their differentiation.

(*i*) **Primary amines** having two available H atoms, react with nitrous acid to form primary alcohols with the evolution of nitrogen (Test).



$$\underset{\text{Primary amine}}{RN\boxed{H_2+O}}=\underset{(HNO_2)}{N-OH} \longrightarrow \underset{\substack{\text{Diazonium}\\\text{salt}\\\text{(Unstable)}}}{RN^+ \equiv NOH^-} \xrightarrow{+H^+} \underset{\text{Carbonium ion}}{R^+} + H_2O + N_2$$

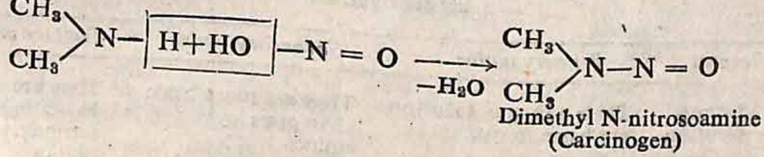
$$R^+ \xrightarrow{HO^-} \underset{\text{Alcohol}}{ROH}$$

Primary aromatic amines (*e.g.*, aniline) react to give the stable aromatic diazonium salts. The diazonium salt from aniline is, however, unstable to heat and is hydrolysed to phenol when heated in water.

$$\underset{\text{Aniline}}{C_6H_5-NH_2} \xrightarrow{HNO_2} \underset{\text{(Unstable)}}{C_6H_5N_2^+\,OH^-} \xrightarrow[\text{Warm}]{H_2O} \underset{\text{Phenol}}{C_6H_5OH}$$

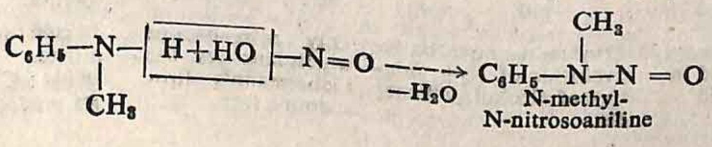
The diazonium salts are versatile intermediates, useful for the synthesis of a number of compounds.

Secondary amines : Both aliphatic and aromatic secondary amines react with nitrous acid to produce neutral, yellow oily product, N-nitrosoamines. The lone hydrogen atom present in these amines is replaced by a nitroso group yielding an N-nitroso-compound. Nitrogen is evolved.



$$(CH_3)_2N-\boxed{H+HO}-N=O \xrightarrow[-H_2O]{} (CH_3)_2N-N=O$$

Dimethyl N-nitrosoamine
(Carcinogen)



$$C_6H_5-N(CH_3)-\boxed{H+HO}-N=O \xrightarrow[-H_2O]{} C_6H_5-N(CH_3)-N=O$$

N-methyl-
N-nitrosoaniline

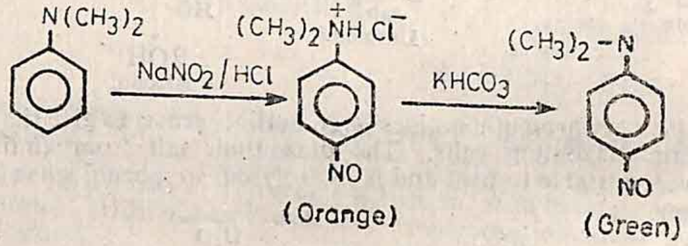
The formation of N-nitrosoamine is used as a test for secondary amines in the Liebermann's nitroso reaction. The nitrosoamine on warming with a crystal of phenol and a few drops of concentrated sulphuric acid yields a blue green solution. On dilution the colour changes to red and changes further to deep blue on treatment with alkali.

Tertiary amines: With aliphatic tertiary amines only normal acid-base reactions occur as there is no replaceable hydrogen.

$$(CH_3)_3N + HNO_2 \longrightarrow \underset{\text{Trimethyl ammonium nitrite}}{[(CH_3)_3NH]^+ NO_2^-}$$

The tertiary amine can be regenerated from the salt solution by addition of alkali.

Aromatic tertiary amines undergo electrophilic aromatic substitution by the NO group at the para-position to give water soluble para-nitroso compounds. The introduction of —N=O group in the benzene ring is called nitrosation.



Differences in behaviour of the three classes of amines with nitrous acid may be used for their distinction.

Distinction between three Classes of Amines

The primary, secondary and tertiary amines can be distinguished from each other on the basis of the following tests. (Table 11.3).

TABLE 11·3. Tests generally employed to differentiate between amines

Reagent	*Primary amine*	*Secondary amine*	*Tertiary amine*
1. Litmus solution	Their aqueous solutions are basic to litmus.	They are more basic than primary amines.	They are more basic than secondary amines.
2. Nitrous acid in cold	**Ethylamine**: quantitative evolution of N_2 + mixture of alcohol, alkene, *etc*.	Oily nitrosoamine which answers the Liebermann's nitrosoamine test.	**In cold** : form nitrites **In hot** : Complex products

Reagent	*Primary amine*	*Secondary amine*	*Tertiary amine*
	In Cold Aniline : Diazonium salt is formed which gives dye test **On warming :** evolution of N_2+phenol		
3. (*i*) Hinsberg's test	Clear solution	Insoluble compound	Insoluble
(*ii*) Acidify	Precipitate appears	Unaffected by acid	Clear solution
4. Chloroform + alcoholic NaOH (carbylamine test)	Offensive smell of carbylamine	No action	No action

11.8. DETECTION OF FUNCTIONAL GROUPS

A. Compounds which do not contain nitrogen :

In such a case the compound may contain one or more of the [following groups : —OH (phenolic or alcoholic); $>C=O$ (carbonyl, —aldehydic and ketonic) ; and —COOH (carboxyl). Perform the tests in the order given below :

Experiment	*Observation*	*Inference*
1. Note the colour and odour of the sample.	...	...
2. Burn a small amount of the sample on a nickel spatula (or, in a test tube).	Sooty flame	Aromatic compounds
3. Shake a small amount of the substance with a little water in a test-tube and test the resulting suspension or solution with litmus paper.	(*i*) Acidic towards litmus.	(*i*) Acids and acidic substances such as some phenols
	(*ii*) Neutral to litmus.	(*ii*) Alcohols, and carbonyl compounds
4. Shake a small amount of the substance with dil. solution of NaOH (5-10%) in a test-tube and warm.	Dissolves.	May be phenols and carboxylic acids
5. Shake a small amount of the substance with a little water ; add a drop of neutral $FeCl_3$ solution to the resulting solution or suspension. Note the change.	(*i*) Violet, blue or green colouration (permanent or transient).	(*i*) Phenolic compounds (phenolic –OH group
	(*ii*) Reddish colouration or precipitate.	(*ii*) May be carboxylic group present.

Experiment	*Observation*	*Inference*
6. Perform the above expt. by adding a drop of neutral $FeCl_3$ solution to an alcoholic solution of the substance.	Violet, blue or green colouration (permanent or transient).	Phenolic compounds (phenolic —OH group

Note : Perform some 'additional tests' given in the text for detection of phenolic compounds.

Experiment	*Observation*	*Inference*
7. Add solid $NaHCO_3$ to the aqueous solution of the compound. In case the compound is insoluble in water, sprinkle the solid sample on $NaHCO_3$ solution.	Effervescence	Carboxylic acids (—COOH group)
8. Add a little (0.1—0.2 g) of the compound to be tested to about 5 mL of a saturated solution of 2 : 4 dinitrophenylhydrazine in HCl. Shake, and if no precipitate appears immediately, heat gently to boiling and continue heating the reaction mixture for 2-3 min in a boiling water bath. Allow it to stand for five minutes. In case no ppt. appears add water dropwise and scratch the walls of the test tube until you get turbidity. Warm, cool and allow to stand.	Yellow, orange or a red ppt.	Carbonyl compounds $\rangle$CO group (aldehydic and/or ketonic groups)

Distinction between an aldehyde and a ketone :

If a carbonyl group in a compound is detected, then it may be either an aldehyde or a ketone. Differentiation between the two may be made by performing the following tests :

Experiment	*Observation*	*Inference*
9. **With Schiff's reagent** : To 2 or 3 mL of Schiff's reagent add a small amount of the original sample. Shake well and allow to stand for two minutes. Note. Don't heat the mixture. Appearance of pink colour is slow in the case of aromatic aldehydes. Some ketones though respond to this test, the reaction is extremely slow. Note that Schiff's reagent is magenta solution, the colour is discharged by sulphur dioxide.	Appearance of pink colour.	Aldehyde
10. **Tollen's reagent** : Add a little of the substance under examination to Tollen's reagent. Shake and warm by placing the test-tube in a boiling water bath.	Formation of a mirror of *silver* or a greyish black ppt.	Aldehyde, [$R\text{-}CHO+Ag_2O=R\text{-}COOH+2Ag$.]
11. **Fehling's solution** : Mix equal volumes of Fehling's solution, A and B. Add a little of the substance under investigation to the mixed	A red ppt. of Cu_2O	**Aldehyde** **$RCHO+2Cu(OH)_2\rightarrow RCOOH+Cu_2O+2H_2O$**

Experiment	*Observation*	*Inference*
solution taken in a test-tube and then warm.		
If the above tests for an aldehyde are negative, then the carbonyl compound is a ketone (*i.e.* it contains a ketonic group).		
Note. The aromatic aldehydes do not reduce alkaline copper salt.		
Of course, Fehling's and ammonical silver nitrate are readily reduced by α-hydroxyketones, *i.e.*, having the grouping —CH(OH)CO—.		
12. Take about 1g of the compond in a dry test-tube. Add a mixture of 4 mL acetic anhydride and two drops of conc. H_2SO_4. Warm in boiling water-bath and then pour the contents into about 15 to 20 mL of water in a beaker. Stir well.	A ppt. or formation of a separate liquid layer (having a plesant smell), which floats on water.	Alcoholic or phenolic compounds (—OH group)
13. Xanthate test. Take in a clean and dry test tube a small amount of the compound and finely powdered KOH approximately in the ratio of 1 : 10 by mass ; warm a little. Now cool and add 5-6 drops of ether and 3-4 drops of CS_2. Shake the mixture (*i*) for about 5 minutes;	(*i*) A yellow ppt.	Alcohol (Alcoholic —OH group)
(*ii*) now add 3-4 drops of 1% ammonium molybdate solution, shake very gently and acidify with dil. H_2SO_4. Add about 10 drops of chloroform and shake.	(*ii*) The chloroform layer becomes violet or reddish-blue.	Alcohol (Alcoholic —OH group)

B. Compounds which contain nitrogen only :

In such a case the compound under examination may contain $-NH_2$ group only. Perform the following experiments in the order given below for detecting the group present :

Experiment	*Observation*	*Inference*
1. Note the colour and odour of the sample.		
2. Shake a small amount of the sample with water in a test-tube and test the resulting solution or suspension with litmus paper.	Neutral	May be some aromatic amino compounds
	Alkaline	Amines (aliphatic and some aromatic)
3. Shake a little of the compound with dil. HCl in a test-tube.	Substance originally slightly soluble or insoluble in water but dissolves in dil. HCl.	Basic substances (*e.g.* Amines)

Experiment	*Observation*	*Inference*
4. **Carbylamine reaction:** Dissolve 0·2g of solid NaOH in 2 mL. alcohol taken in a test-tube. Now add a little of the compound, two or three drops of chloroform and warm gently.	A characteristic obnoxious odour.	Aliphatic or aromatic amino compounds. ($-NH_2$ group)
5. **Diazo reaction and coupling.** Dissolve a little of the sample in dil HCl, cool and add in lots a cold aqueous solution of sodium nitrite. Cool the solution again and pour a little of it into an excess of cold alkaline solution of β-naphthol.	An immediate brilliant scarlet red precipitate or colouration.	Aromatic amino compound (aromatic $-NH_2$ group).

Notes on detection of functional groups

1. **Colour and odour**. The colour and odour of the organic compound should always be noted. It may sometimes be help to make out the class to which the compound under examination belongs. For example, nitro compounds are generally yellow (pale or deep) or orange coloured. Hydrocarbons, alcohols, phenols, aldehydes, ketones and acids are generally colourless. Esters, alcohols and aromatic hydrocarbons may have sweet and pleasant smell. Pungent and irritating odours are given by lower aliphatic acids, acid halides, *etc*. Phenols, lower aliphatic ketones, *etc*. possess characteristic smell. It is, however, a matter of practice to identify the type of odour of a substance under investigation.

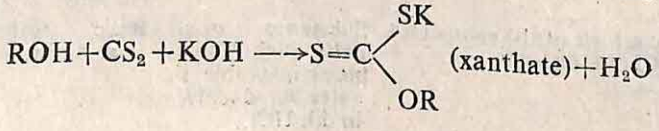
2. The colour shown by some of the phenolic compounds on reaction with ferric chloride solution is very much transitory in nature. Hence, the colour should be noted immediately after addition of $FeCl_2$ solution.

3. Not only the compounds containingg $-COOH$ group give effervescence with $NaHCO_3$ but there are others such as chlorophenols, nitrophenols, amine salts, *etc*. easily give sufficiently strong acid reactions to produce effervescence with $NaHCO_3$.

4. 2 : 4-Dinitrophenylhydrazine forms 2 : 4-dinitrophenylhydrazone with carbonyl compounds (*i.e*. compounds containing $>C=O$ group).

$$>CO + H_2N\text{-}NHC_6H_2(NO_2)_2 \longrightarrow \underset{\text{2:4-Dinitrophenylhydrazones}}{>C=N\text{-}NH\text{-}C_6H_3(NO_2)_2} + H_2O$$

5. The yellow ppt. is due to xanthate. It is formed when alkoxide obtained from alcohol and KOH reacts with CS_2



$$ROH + CS_2 + KOH \longrightarrow S=C\begin{cases} SK \\ OR \end{cases} \text{(xanthate)} + H_2O$$

With ammonium molybdate, xanthate in slightly acidic solution forms a coloured complex.

6. The presence of ethyl alcohol is confirmed by iodoform test. With iodine and caustic alkali, ethyl alcohol forms iodoform.

$$C_2H_5OH+4I_2+6NaOH \rightarrow CHI_3+HCOONa+5NaI+5H_2O.$$

7. Both aliphatic and aromatic amines give carbylamine reaction. This reaction is also called isocyanide reaction.

$$Ar\text{-}NH_2+CHCl_3+3KOH \rightarrow \underset{\text{Aryl isocyanide}}{ArNC}+3KCl+3H_2O$$

[When Ar stands for an aryl group; hence $ArNH_2$ is an aromatic amine.]

$$\text{Similarly, } R\text{-}NH_2+CHCl_3+3KOH \rightarrow \underset{\text{Alkyl isocyanide}}{RNC}+3KCl+3H_2O$$

[Where R stands for an alkyl group and hence $R\text{-}NH_2$ is an aliphatic amine.]

8. Salts of aromatic primary amino compounds react with nitrous acid ($NaNO_2+HCl$) in the cold to produce soluble diazonium salts. This reaction is **diazo reaction.** [During diazotisation temperature should be kept between 0°C—5°C and an aqueous solution of sodium nitrite should be added in lots, until the reaction mixture produces a blue colour with KI—starch paper.] The diazonium salt so produced couples with phenols and other aromatic hydroxy derivatives in **alkaline** medium to give brilliant coloured azo-dyes. With aniline, for example, the reaction is :

$$C_6H_5NH_2HCl+HONO \longrightarrow \underset{\text{Diazo-salt}}{C_6H_5N{=}NCl}+2H_2O$$

$$C_6H_5N{=}NCl+\underset{\beta\text{-Naphthol}}{C_{10}H_7OH} \longrightarrow \underset{\text{A scarlet azo-dye}}{C_6H_5N{=}NC_{10}H_6OH}+HCl$$

ORAL QUESTIONS AND ANSWERS

Q. 11.1. What is a functional group ?

Ans. A group of atoms that show characteristic properties of the organic compound.

Q. 11.2. What is the significance of functional groups ?

Ans. They help in identifying the various families of organic compounds.

Q. 11.3. What are unsaturated hydrocarbons ?

Ans. The organic compounds which contain double bonded $>C=C<$ and/or triple bonded $-C\equiv C-$ carbon atoms are called the unsaturated compounds.

Q. 11.4. What is the characteristic reaction of an unsaturated compound and of a saturated compound ?

Ans. Saturated compounds undergo substitution reactions whereas unsatutated compounds undergo addition reactions.

Q. 11.5. Name the usual reactions used to detect unsaturation of an organic compound.

Ans. Reactions of bromine and alkaline potassium permanganate.

Q. 11.6. What is Baeyer's reagent ?

Ans. It is a 1% cold alkaline solution of potassium permanganate in water. It is made alkaline with sodium carbonate.

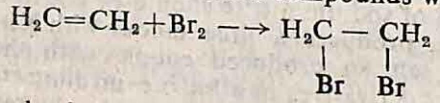
Q. 11.7. Iodine and chlorine solutions are not used to detect the unsaturation of organic compounds. Comment.

Ans. The reaction of iodine is too slow. Hence it is not used.

Chlorine solultion is considered to be corrosive. Its colour is not distinct, hence difficult to make out its addition on the basis of colour.

Q. 11.8. Comment on the reaction of bromine with ethylene.

Ans. Bromine forms addition compounds with ethylene.



$$H_2C{=}CH_2 + Br_2 \longrightarrow \underset{\displaystyle Br}{\underset{|}{H_2C}} - \underset{\displaystyle Br}{\underset{|}{CH_2}}$$

HBr is not evolved during the reaction. Addition of bromine is usually carried out in chloroform, carbon tetrachloride or acetic acid media. For water soluble compounds aqueous solution can also be used.

Q. 11.9. The alkaline potassium permanganate reaction it not considered a very reliable reaction for the detection of unsaturation. Comment.

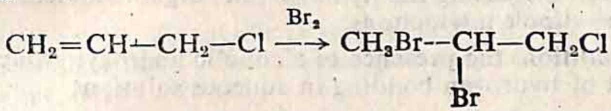
Ans. The discharge of colour of permanganate ions is due to their reduction to colourless manganese (II) ions. Any reducing agent can, therefore, discharge the colour of potassium permanganate solution. Hence, this reaction alone is not considered a reliable reaction to detect the unsaturation in the compound. However, this reactson provides support to the findings of the bromime reaction.

Q. 11.10. What happens when bromine is added to benzene C_6H_6 ?

Ans. Benzene contains three double bonds. The delocalization of the π (pi) orbital electrons provides a high stability to the molecule. As a result, benzene does not undergo any addition reaction. This could be understood from the colour of bromine solution.

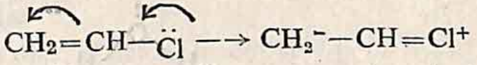
Q. 11.11. Will bromine react with (*a*) allyl chloride, and (*b*) vinyl chloride ?

Ans. (*a*) With allyl chloride, bromine reacts giving addition compound.



$$CH_2{=}CH{-}CH_2{-}Cl \xrightarrow{Br_2} CH_2Br{-}\underset{\displaystyle Br}{\underset{|}{CH}}{-}CH_2Cl$$

(*b*) With vinyl chloride $CH_2{=}CH{-}Cl$, bromine does not form any addition compound due to the resonance in the molecule. Change in the position of double bond takes place.



$$CH_2{=}CH{-}\ddot{Cl} \longrightarrow CH_2^{-}{-}CH{=}Cl^{+}$$

Q. 11.12. At times when bromine reaction is done with unsaturated compounds a white or yellowish precipitate is obtained, especially in aqueous medium. Comment.

Ans. The addition compounds of bromine with organic compounds have generally a lower solubility than the parent compound. Hence the bromo compound may get separated as ppt.

Q. 11.13. How will you make out whether the bromine has reacted or not ?

Ans. From the change in the intensity of colour of bromine solution.

Q. 11.14. Why is sodium metal kept under kerosene oil ?

Ans. To prevent its reaction with air and moisture. Sodium reacts with air forming oxide and carbonate. At times, if the moisture is too much, it catches fire because of the evolution of H_2 gas.

Q. 11.15. Why can't the test with sodium alone be taken as the confirmatory test for alcoholic hydroxyl group ?

Ans. Sodium metal reacts with compounds containing carboxylic (—COOH), phenolic (—OH) and alcoholic (—OH) groups. It also reacts with ketonic compounds with a hydrogen atom attached to the β-carbon atom. Hydrogen gas is evolved in all the cases.

Q. 11.16. Why is calcium chloride added to the organic compounds before adding sodium metal to identify the hydroxyl group ?

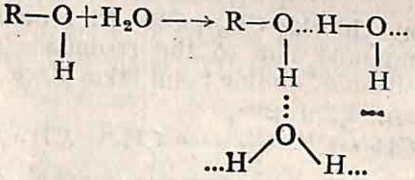
Ans. Calcium chloride is used to absorb moisture and water from the solvent and the organic compound. In the absence of $CaCl_2$, sodium metal will react with water giving a stream of hydrogen :

$$2H_2O + 2Na \longrightarrow 2NaOH + H_2$$

Q. 11.17. How does the presence of hydroxyl group increase the solubility of the compound in water ?

Ans. The —OH group imparts a polarity in the compound. This helps in increasing the hydration of organic molecules through the dipole—dipole interactions.

In addition, the presence of alcohòlic hodroxyl group increases the extent of hydrogen bonding in aqueous solutions



Q. 11.18. How is it confirmed whether the given compound is aliphatic or aromatic ?

Ans. If the compound burns with a smoky flame the compound is aromatic. The higher percentage of carbon is responsible for smoky flame. If the compound burns with a non-smoky flame, the compound is aliphatic.

Q. 11.19. Where is ceric ammonium nitrate reagent employed ?

Ans. It is employed for the identification of alcohols and phenols. A red colour is obtained in case of alcohols whereas brown (or green) ppt. is obtained with phenols.

Q. 11.20. What is the reaction of carboxylic acids and phenols with iron (III) chloride solution ?

Ans. With $FeCl_3$, phenolic compounds give deep violet, blue or green coloured complexes. With carboxylic acids, iron (III) gives deep red coloured carboxylate salts. Carboxylates on boiling get hydrolysed forming reddish brown precipitate of the basic salts. For example,

$$FeCl_3+3CH_3COOH \longrightarrow Fe(OCOCH_3)_3+3HCl$$

$$Fe(OCOCH_3)_3+H_2O \longrightarrow \underset{\text{Red brown ppt.}}{FeO(OCOCH_3)}+2CH_3COOH$$

Q. 11.21. Does sodium bicarbonate react with carboxylic acid and phenol on the same lines ?

Ans. Carboxylic acid reacts with $NaHCO_3$ as below :

$$CH_3COOH+NaHCO_3 \longrightarrow CO_2+H_2O+CH_3COONa$$

Since in the resonance stabilized benzoate anion the negative charge is on oxygen and not on carbon (as in the resonance forms of phenoxide) this is stabilized to a greater extent and hence benzoic acid will be a stronger acid than phenol. Benzoic acid, therefore, will release carbon dioxide from sodium bicarbonate while phenol will not do so.

Q. 11.22. Both phenols and alcohols contain —OH group. How can it be ascertained that the given compound is alcohol or phenol ?

Ans. Phenols are acidic in nature and turn blue litmus red whereas alcohols cannot. Phenols also give deep colour with ferric chloride while alcohols do not.

Q. 11.23. Suggest a few tests which could be employed to differentiate between phenol and ethanol.

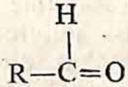
Ans. 1. **Ferric chloride test.** Phenol gives violet colour with ferric chloride.

2. **Litmus test.** Phenol bring acidic in nature turns blue litmus red.

3. **Iodoform test.** Ethanol forms yellow ppt. of iodoform.

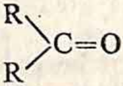
Q. 11.24. What are carbonyl compounds ? What is the difference between aldehyde and ketone ?

Ans. Carbonyl compounds contain the $>C=O$ group attached to two alkyl group or hydrogen atoms. In aldehyde, $>$**CO** is essentially attached to one hydrogen atom, whereas in a ketone $>CO$ is attached to two alkyl groups.



$R-\overset{\overset{\displaystyle H}{|}}{C}=O$

Aldehyde



Ketone

Q. 11.25. Suggest the name of a characteristic reagent to detect $>C=O$ in a compound.

Ans. 2, 4-Dinitrophenylhydrazine.

Q. 11.26. Name a few reagents which can distinguish between an aldehyde and a ketone.

Ans. (*i*) Tollen's reagent

(*ii*) Fehling's solution.

Refer to Section 11.5.5.

Q. 11.27. What is Tollen's reagent ? Give its use in organic analysis.

Ans. It is a colourless solution. It is obtained by adding caustic soda drop by drop to a solution of silver nitrate. As a result, a grey ppt. of AgOH is obtained which is dissolved in excess of aqueous ammonia solution.

$$AgNO_3 + NaOH \longrightarrow \underset{\text{(White ppt.)}}{AgOH} + NaNO_3$$

$$2AgOH \longrightarrow Ag_2O + H_2O$$

$$Ag_2O + 4NH_4OH \longrightarrow \underset{\text{(Colourless)}}{2[Ag(NH_3)_2]^+OH^-} + 3H_2O$$

It is used to make a distinction between an aldehyde and a ketone. With Tollen's reagent, aldehydes give a silver mirror or greyish black ppt. of Ag whereas ketones do not.

$$RCHO + [Ag(NH_3)_2]^+ + 3OH^- \longrightarrow RCOO^- + \underset{\text{Silver mirror}}{2Ag} + 4NH_3 + 2H_2O$$

Q. 11.28. What is Fehling's solution ? Give its use in organic analysis.

Ans. It is prepared by mixing two solutions say A and B. Solution A contains copper sulphate whereas solution B contains Rochelle salt (sodium potassium tartrate) and aqueous sodium hydroxide.

The reagent is employed to distinguish between aldehydes and ketones. Aldehydes when heated with Fehling's solution yield red ppt. of cuprous oxide whereas ketones do not.

$$RCHO + 2Cu^{2+} + 5OH^- \longrightarrow RCOO^- + 2H_2O + \underset{\text{(Red ppt.)}}{Cu_2O}$$

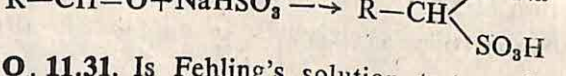
Q. 11.29. What is Schiff's reagent ? Suggest its use in organic analysis.

Ans. It is prepared by dissolving rosaniline hydrochloride (dye) in water. As a result, a pink coloured solution is obtained. The pink colour is discharged by passing sulphur dioxide gas. It is used to detect aldehydes.

The reagent is always added to a cold solution of an aldehyde. In the hot medium sulphur dioxide is released and the pink colour reappears. This may mislead the inference.

Q. 11.30. What happens when an aldehyde is heated with an aqueous solution of $NaHSO_3$?

Ans. With $NaHSO_3$, aldehydes give addition compounds. Such compounds are obtained from the reaction mixture as white crystalline solids.



$$R{-}CH{=}O + NaHSO_3 \longrightarrow R{-}CH\begin{cases} O^-Na^+ \\ SO_3H \end{cases}$$

Q. 11.31. Is Fehling's solution test applicable to aromatic aldehydes ?

Ans. Fehling's test is positive for aliphatic aldehydes whereas aromatic aldehydes do not respond to the test.

Q. 11.32. The sodium bicarbonate test is generally carried out for the detection of —COOH group. Is this test also given by some other compounds ?

Ans. Yes. A few phenolic compounds like 2, 4, 6- trinitrophenol (picric acid), *etc.* also give effervescene with sodium bicarbonate.

Q. 11.33. Can a solution of sodium carbonate be used to detect —COOH group ?

Ans. No. Sodium carbonate is more alkaline than sodium hydrogen carbonate, and is decomposed by both carboxylic acids and phenols.

Q. 11.34. How are carboxylic acids detected in the regular analysis ?

Ans. 1. The —COOH group is detected by $NaHCO_3$. Brisk effervescence with evolution of CO_2 confirms —COOH group.

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + CO_2 + H_2O$$

Phenols do not decompose $NaHCO_3$ solution. Both phenols and carboxylic acids turn blue litmus red.

2. Carboxylic acids on refluxing with ethanol in presence of conc. H_2SO_4 or anhydrous $ZnCl_2$ give sweet smelling esters.

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \overset{H^+}{\rightleftharpoons} \underset{\substack{\text{Ethyl acetate} \\ \text{(Ester)}}}{CH_3COOC_2H_5} + H_2O$$

Q. 11.35. Which functional group is tested with carbylamine reaction ?

Ans. Amino, $-NH_2$, group. Amines on heating with a small amount of conc. HCl, chloroform and alcoholic potassium hydroxide solution produce isocyanides (carbylamine) possessing very offensive smell.

Q. 11.36. Do amino acids give carbylamine reaction ?

Ans. This reaction is successful for primary amines only. This reaction is not successful for amino acids because no odour is detected due to non-volatility of the isocyanide formed with them.

Q. 11.37. Suggest the test by which primary aromatic amine is identified.

Ans. Azo-dye test.

Q. 11.38. What is Hinsberg's test ?

Ans. Hinsberg's test is used to identify and separate primary, secondary and tertiary amines.

□ □

UNIT 12

Distinction Between Pairs Of Organic Compounds

12.1. INTRODUCTION

We have discussed in Unit 11 about the various tests which could successfully be employed in identifying the various functional groups. It is the presence of functional groups in the organic compounds that produces the dominant chemical characteristics of substances. However, at times, these tests may not be helpful in distinguishing two compounds with the same functional groups. In this unit, we will discuss the various aspects which could lead to distinction between the following pairs of organic compounds.

—methanol and ethanol

—benzaldehyde and acetone

—ethyl alcohol and phenol

—phenol and benzoic acid

—aniline and phenol

12.2. DISTINCTION BETWEEN METHANOL AND ETHANOL

1. General

Methyl alcohol is a colourless, neutral, volatile and inflammable liquid with a pungent smell. It is miscible with water in all proportions.

Ethyl alcohol is a colourless, neutral, volatile and inflammable liquid with a characteristic pleasant and sweet smell. It is miscible with water in all proportions :

—Both the alcohols react with sodium metal with effervescence. Hydrogen gas is evolved.

—Both give pink or red colouration with ceric ammonium nitrate.

—Both react with carboxylic acids in the presence of conc. H_2SO_4 producing sweet smelling esters.

2. **Oxidation with copper coil** (Refer to Text Book). Both methanol and ethanol are primary alcohols. They on oxidation form different products.

Methyl alcohol on oxidation gives formaldehyde which can be tested by its usual tests.

Ethyl alcohol on oxidation gives acetaldehyde which can be tested by its usual tests.

3. **Iodoform test.** Ethanol is easily oxidized to acetaldehyde, CH_3CHO which contains CH_3CO—group. Hence, this alcohol should undergo iodoform reaction. Methanol, on the other hand is oxidized to HCHO and will not undergo iodoform reaction.

$$CH_3CH_2OH \xrightarrow{I_2/NaOH} CHI_3$$

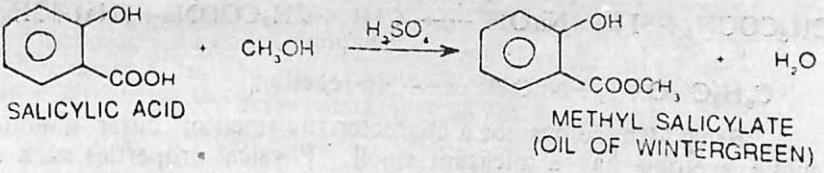
$$CH_3OH \xrightarrow{I_2/NaOH} \text{Iodoform is not formed}$$

Take 0.5 mL of the alcohol in a test tube. Add 1 mL 1.0% iodine solution in KI followed by caustic soda solution (5.0%) of drop by drop until the brown colour of iodine is discharged. Warm gently in a boiling water bath.

—Appearance of crystalline yellow ppt. with a characteristic odour confirms the presence of ethanol.

4. **Oil of wintergreen test.** Take ~0.1 g of salicylic acid or its sodium salt in a test tube. Add 1 mL of alcohol and a few drops of conc. H_2SO_4. Heat gently in a boiling water bath and cool.

A characteristic odour confirms the prerence of methanol.



Ethyl salicylate has no characteristic odour.

5. **Boiling point.** Methanol boils at 59°C and ethanol boils at 78°C. We have already learnt about the technique of determining boiling points of liquids in Class XI.

S. No.	Experiment	Methane	Ethane
1.	State and colour of the compound	Colour less liquid	Colourless liquid
2.	Boiling point	59° C	78° C
3.	Frame test	Burns with non-luminous flame ; oriphatic in nature.	Burns with non-luminous flame ; aliphatic in nature.
4.	Iodoform test (Refer to Section 11·54).	No yellow ppt. appears.	Yellow ppt. appears.
5.	Oil of winter green test	Methyl solieylate is formed. It has a characteristic odour	Ethyl solicylate, it has no characteristic odour

12.3. DISTINCTION BETWEEN BENZALDEHYDE AND ACETONE

Both benzaldehyde and acetone contain a carbonyl group (>C=O). Benzaldehyde has an aldehydic group while acetone has a ketonic group. These two compounds can be distinguished by performing some specific tests both for aldehydes and ketones given in Unit II (Refer to Sections 11.5.3, 11.5.4 and 11.5.5) *e.g.*, aldehydes reduce Tollen's reagent and Schiff's reagent whereas ketones do not reduce these reagents.

$$C_6H_5CHO+\underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]+OH}\longrightarrow C_6H_5COOH+\underset{\text{Silver mirror}}{2Ag}+H_2O+4NH_3$$

$$CH_3COCH_3+[Ag(NH_3)_2]OH\longrightarrow \text{No reaction}$$

Acetone contains $CH_3CO—$ group, hence it is expected to undergo reaction whereas benzaldehyde will not undergo this reaction.

$$CH_3COCH_3+3I_2+4NaOH\longrightarrow \underset{\text{Iodoform}}{CHI_3}+CH_3COONa+3NaI+3H_2O$$

$$C_6H_5CHO+I_2+NaOH\longrightarrow \text{No reaction}$$

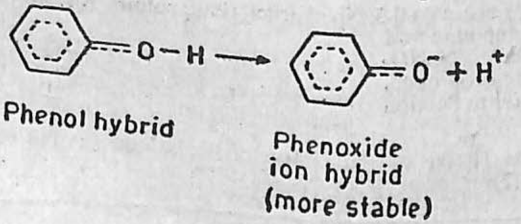
Benzaldehyde has got a characteristic smell of bitter almonds while acetone has a pleasant smell. Physical properties such as boiling point solubility, etc. can also be used to distinguish between these two compounds.

S.No.	*Experiment*	*Obseration*	
		Acetone	*Benzaldehyde*
1.	State and colour of the compound.	Colourless liquid.	Colourless liquid
2.	Smell of the compound.	Characteristic sweet smell	Smell of bitter almonds
3.	Solubility		
	(i) In water	Miscible	Immiscible
	(ii) In ethanol	Miscible	Miscible
4.	Flame test	Non-sooty flame aliphatic compound	Sooty flame; aromatic compound.
5.	Boiling point	56°C	179°C
6.	2,4 Dinitophenylhydrazine test. (Refer to Section 11.5.2)	Yellow precipitate, mp 128°C	Yellow precipitate, mp 235°C.
7.	Test with Tollen's reagent (Refer to Section 11.5.3).	No silver mirror	Silver mirror is formed.
8.	Test with Schiff's reagent (Refer to Section 11.5.3)	No pink colour	Pink colour appears
9.	Iodoform test (Refer to Section 11.5.4)	Yellow ppt. is formed	No Yellow ppt.

12.4. DISTINCTION BETWEEN ETHYL ALCOHOL AND PHENOL

Both phenol and ethanol contain —OH groups. In ethanol —OH is attached to an alkyl part and in phenol, —OH is attached to a benzene ring.

Phenol is acidic in nature and gives colouration with $FeCl_3$ solution. If loses proton to yield phenoxide ion whose resonance hybrid is much more stable than the resonance hybrid of phenol itself. Thus phenol residue becomes more stable after releasing H^+. This accounts for the acidic behaviour of phenol.



Alcoholic —OH group has neither acidic nor basic characteristics in aqueous solution. It does not give any characteristic colour with $FeCl_3$. Ethanol releases a H^+ forming ethoxide ion which is not stabilized by resonance.

Phenol has characteristic astringnic smell and ethanol has pleasant and sweet smell. Other physical proporties like bp, colour, solubility, *etc.* can also be used to distinguish between the two compoundsl

Then two liquids can also be distinguished by performing iodoform test, *etc.*

S.No.	*Experiment*	*Observation*	
		Ethanol	*Phenol*
1.	Physical state and colour of the compound	Colourless volatile liquid	Colourless or pinkish (due to aerial oxidation) solid which melts to reddish coloured liquid.
2.	Solubility in water	Miscible in all proportions	Limited solubility; forms two layers in concentrated solution.
3.	Flame test	Non-sooty, non-luminous flame : aliphatic compound	Sooty, luminous flame: aromatic compound.
4.	Melting or boiling point	$bp = 78°C$	$mp = 43°C$, $bp = 181°C$
5.	Litmus test	Netural	Acidic ; turns blue litmus red
6.	Neutral ferric (III) chloride test (Refer to Section 11.4.2)	No green violet or blue colour	Violet colour appears
7.	Reaction with bromine water. To 1 mL aqueous solution of the compound add bromine water drop by drop. Note the compound formation	No reaction	White precipitate of tribromophenol
8.	Iodoform test (Refer to Section 11.5.4)	Yellow precipitate of iodoform	No reaction
9.	Liebermann's test : To 0.5 mL of the compound add a few crystals of $NaNO_2$ and a few drops of conc. H_2SO_4. (Refer to Section 11.4.2)	No characteristic colour	A green or blue colour
10.	Phthalein test (Refer to Section 11.4.2)	No characteristic colour	A red colour

12.5. DISTINCTION BETWEEN PHENOL AND BENZOIC ACID

Both phenol and benzoic acid are aromatic in nature. They are acidic in nature as they release proton. The respective anions (conjugate bases) are resonance stabilized (Refer to standard text book). However, with $NaHCO_3$, only benzoic acid gives efferevescence, while phenol, being a weaker acid in nature, does not react with $NaHCO_3$.

Benzoic acid is a colourless, plate like or needle shaped crystalline solid. It is sparingly soluble in cold water but more soluble in hot water.

Phenol is a colourless, crystalline low melting solid. It has a characteristic carbolic smell. It is sparingly soluble in water. It dissolves readily in alkali.

S.No.	*Experiment*	*Observation*	
		Phenol	*Benzoic acid*
1.	Physical state and colour	Colourless or pink coloured solid which melts.	White crystalline solid
2.	Solubility		
	(i) in water	Sparingly soluble	Sparingly soluble
	(ii) in dil NaOH	Soluble	Soluble.
3.	Melting po'nt	43°C	12.1.5°C
4.	Blue litmus test	Turns red .	Turns red
5.	Reaction with $NaHCO_3$ solution. Warm if necessary	No effervescence	Strong effervescence. CO_2 is evolved (Test with lime water)
6.	Neutral $FeCl_3$ solution test (Refer to Section 11.4.2)	Violet colour	A buff coloured ppt. Souble in dil. HCl White solid reappears
7.	Liebermann's reaction (Refer to Section 11.4.2)	Deep blue or green colour.	No colouration
8.	Ester formation test (Refer to Section 11.3.2)	—	Pleasant sweet smell due to ester

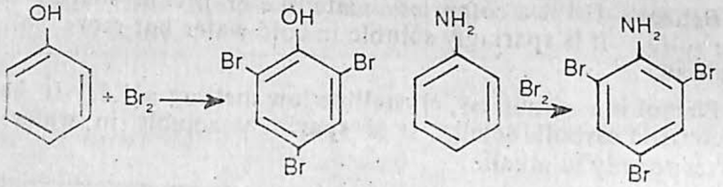
12.6. DISTINCTION BETWEEN ANILINE AND PHENOL

Aniline is an amino compound while phenol contains —OH group. The two compounds can be distinguished by performing the specific tests for the phenolic group (Liebermann's and ferric chloride tests) and the amino group (solubility in HCl, azodye and carbylamine tests). Aniline is basic in nature due to the presence of a lone pair of electrons on nitrogen.

Phenol, on the other hand, is acidic in nature.

Freshly distilled aniline is a colourless oily liquid. If turns reddish brown when exposed to light and air. It is slightly soluble in water. If forms crystalline salts with acids. It has a characteristic odour (nauseating). Both phenols and aniline react in a similar manner as illustrated below :

(*i*) **Bromination**



Take 0.5 mL of the liquid in a test-tube. Add ~5 mL water. Now add bromine water drop by drop and shake. White solid separates.

(*ii*) Both phenol and aniline can be acetylated and benzoylated with acetyl chloride and benzoyl chloride respectively.

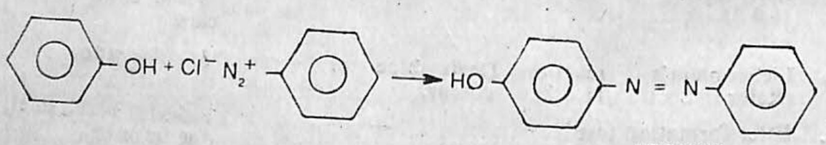
$$C_6H_5NH_2 + ClCOCH_3 \longrightarrow C_6H_5NHCOCH_3 + HCl$$

$$C_6H_5OH + ClCOCH_3 \longrightarrow C_6H_5OCOCH_3 + HCl$$

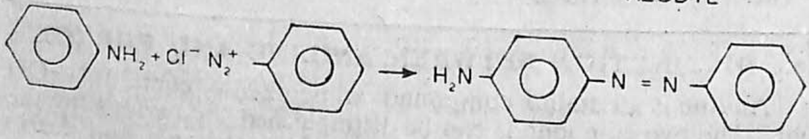
$$C_6H_5NH_2 + C_6H_5COCl \longrightarrow C_6H_5NHCOC_6H_5 + HCl$$

$$C_6H_5OH + C_6H_5COCl \longrightarrow C_6H_5OCOC_6H_5 + HCl$$

(*iii*) Both aniline and phenol undergo coupling reaction with diazonium salts and produce azo compounds. These reactions form the basis of azodye formation.



AZODYE



Aniline yellow

S.No.	Experiment	Observation	
		Phenol	*Aniline*
1.	Physical state and colour.	Colourless or light pink solid which melts.	Reddish brown liquid.
2.	Solubility		
	(i) Water	Sparingly soluble	Slightly soluble
	(ii) HCl	—	Form salt
	(iii) NaOH	Soluble	
3.	Boiling point	181°C	183°C
4.	Litmus test	Turns blue litmus red	Turns red litmus blue
5.	Neutral ferric chloride test	Violet colouration	No colour
6.	Carbylamine test (Refer to Section 11.7.1)	—	A characteristic obnoxious smell
7.	Azodye test (Refer to Section 11.7.2)	No scarlet-red dye is formed	Scarlet red ppt. of the azodye
8.	Liebermann's test (Refer to Section 11.4.2)	Deep blue or green colour	—

ORAL QUESTIONS AND ANSWERS

Q. 12.1. How can methanol be distinguised from ethanol ?

Ans. Ethanol gives iodoform test while methanol does not.

Q. 12.2. Why does methanol not give iodoform test ?

Ans. It does not contain the essential group, *i.e.* $CH_3CH(OH)$ or CH_3CO required for the iodoform test.

Q. 12.3. Name the compounds which give iodoform test with NaOH+iodine solution.

Ans. All the organic compounds with $-COCH_3$ group or which can be converted into this terminal $-COCH_3$ group give the iodoform reaction. Compounds which contain this group are CH_3CHO, acetaldahyde ; CH_3COCH_3, acetone ; $CH_3COCH_2CH_3$, 2-butanone; $CH_3CH_2CHOHCH_3$, 2-butanol (can be readily oxidized to $CH_3CH_2COCH_3$).

Q. 12.4. Which of the three butyl alcohols, *i.e.* primary, secondary and tertiary will give idoform tests ?

Ans. Only secondary butyl alcohol. This alcohol on oxidation will give $CH_3CH_2COCH_3$.

Q. 12.5. Why does acetone give a blue flame whereas benzaldehyde gives a sooty flame ?

Ans. Benzaldehyde is an aromatic compound whereas acetone is an aliphatic compound.

Q. 12.6. Name one property which has been the basis of distinction between benzaldehyde and acetone.

Ans. Reducing behaviour of benzaldehyde and non-reducing behaviour of acetone.

Q. 12.7. Does benzaldehyde reduce Fehling's solution ?

Ans. Benzaldehyde does not reduce Fehling's solution—a distinction from acetaldehyde.

Q. 12.8. Phenol is acidic while ethanol is not. Comment.

Ans. (Refer to Section 12.4).

Q. 12.9. Which of the two, benzoic acid and phenol, is more acidic and why ?

Ans. (Refer to Section 12.5).

Q. 12.10. Benzaldehyde gives a Tollens' reagent test but acetone does not. Comment.

Ans. (Refer to Section 12.3).

Q. 12.11. What are the chemical similarities between ethanol and phenol ?

Ans. (1) Both contain —OH groups. Both react with sodium metal and evolve hydrogen,

$$2C_2H_5OH+2Na \longrightarrow 2C_2H_5ONa+H_2$$
$$2C_6H_5OH+2Na \longrightarrow 2C_6H_5ONa+H_2$$

(2) Both form esters with the acyl chloride :

$$C_2H_5OH+CH_3COCl \longrightarrow CH_3COOC_2H_5+HCl$$
$$C_6H_5OH+CH_3COCl \longrightarrow C_6H_5OCOCH_3+HCl$$

Q. 12.12. Suggest the test which can distinguish between ethanol and phenol.

Ans. Phenolic —OH group is acidic in nature. It turns blue litmus red. It gives characteristic violet colour with neutral $FeCl_3$. Alcohol does not give these tests.

Q. 12.13. At times the sample of phenol looks slightly pink in colour. Comment.

Ans. Pure phenol is colourless, It turns pink when exposed to air due to aerial oxidation.

Q. 12.14. Both phenol and benzoic acid turn blue litmus red but with $NaHCO_3$ behave differently. Comment.

Ans. Phenol is a weak acid as compared to benzoic acid.

Q. 12.15. Name some of the common reactions possible in the case of both aniline and phenol.

Ans. (*i*) Bomination, (*ii*) acylation, and (*iii*) coupling reaction of the diazonium compounds.

□□

UNIT 13

Preparation of Organic Compounds

13.1. INTRODUCTION

Organic reactions which lead to the formation of important compounds require special attention. Generally the organic reactions are slow and do not proceed to completion. At times, certain undesirable products are also obtained. Obviously the reactions require proper conditions and techniques so as to get the desired and pure product in adequate yield. We are already familiar with the various methods usually employed in isolating and purifying the organic products (Class XI, Practical Book). In this unit we will study in details about the preparation of the following compounds :

—iodoform

—aspirin

—acetanilide

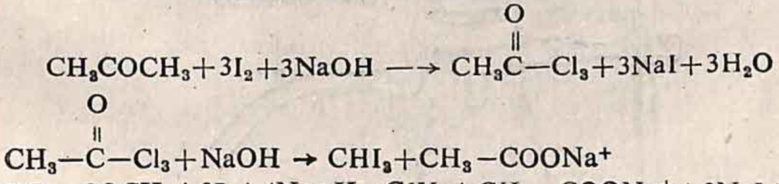
—dibenzal acetone

—p-nitroacetanilide

13.2. IODOFORM, CH_3I

Iodoform is generally prepared by the action of iodine on acetone or ethanol. The reaction is carried out in alkaline medium.

The reaction involves conversion of acetone to tri-iodo-acetone followed by its hydrolysis to iodoform.



$$CH_3COCH_3+3I_2+3NaOH \longrightarrow CH_3\overset{\overset{O}{\|}}{C}-Cl_3+3NaI+3H_2O$$

$$CH_3-\overset{\overset{O}{\|}}{C}-Cl_3+NaOH \rightarrow CHI_3+CH_3-COONa^+$$

$$CH_3-COCH_3+3I_2+4NaOH \rightarrow CHI_3+CH_3-COONa^+ +3NaI+3H_2O$$

Ethyl alcohol, if taken, is first oxidized to acetaldehyde (CH_3CHO), which, in turn, reacts to form iodoform (CHI_3) :

$$CH_3CH_2OH+I_2+2NaOH \rightarrow CH_3CHO+2NaI+2H_2O$$

$$CH_3CHO+3I_2+3NaOH \rightarrow I_3C-CHO+3NaI+3H_2O$$

$$I_3C-CHO+NaOH \rightarrow \underset{\text{Iodoform}}{CHI_3} + HCOONa$$

Acetone is always preferred as its give more yield. It does not involve oxidation to acetaldehyde as with ethanol.

Apparatus : Conical flasks (250 mL), beakers, round bottom flask, water condenser, glass rod, water pump, filtration assembly, water bath, measuring cylinder, filter paper, funnel, boiling tubes.

Chemicals : Acetone (2 mL), potassium iodide (8.0 g), 10% sodium hydroxide (15 mL), 1 M sodium hypochlorite 100 mL, methylated spirit.

Procedure : Place a solution of 8 g of potassium iodide in 50 mL of water in a 250 mL conical flask. Add 20 mL of acetone and 20 mL of 10% sodium hydroxide solution and then slowly add with stirring a freshly prepared solution of sodium hypochlorite until the precipitate of iodoform keeps forming. Allow to stand for 10 minutes. Wash the precipitate twice with water. Yield of crude will be approx. 3.0 g.

You will find that the yellow crystals of iodoform separate out. Separate the product by filtration at the pump (Fig. 13.1).

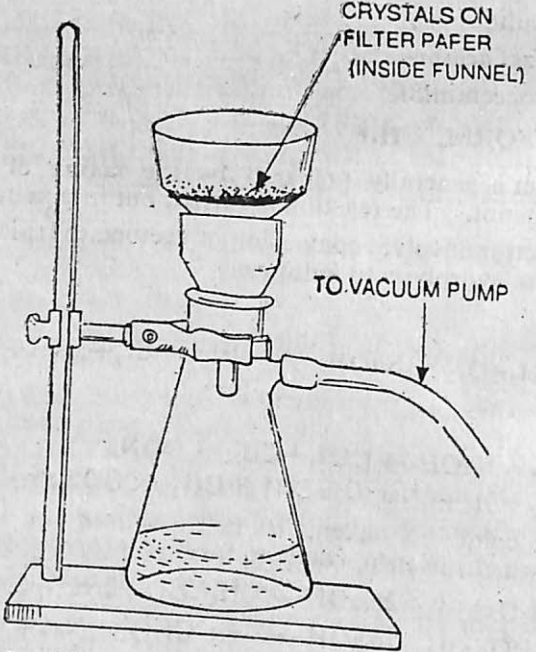


Fig. 13.1. Filtration washing and drying of the crystals on a vacuum filtration assembly with buchner funnel

$$CH_3COCH_3 \xrightarrow[aq]{NaOCl+KI} Cl_3COCH_3 \xrightarrow[aq]{NaOH} CH_3COONa + CHI_3$$

Recrystallize the crude iodoform using methylated spirit. For recrystallization, place the crude iodoform in a 100 mL round-bottom flask fitted with a water condenser. Add a small quantity of mehtylated-spirit and heat to boiling on water bath (Fig. 13.2). Continue addition of small quantities of methylated spirit until all the iodoform has dissolved. Filter the hot solution through a fluted filter paper (Class XI—practical book) into a conical flask and cool. The iodoform crystallizes rapidly. Filter and drain at the pump and allow to dry. (Fig. 13·1). Crystals can be dried by spreading over the folds of filter paper.

Results : Colour of the crystals :
Shape ,, ,, :
Yield ,, ,, :
mp ,, ,, : (Literature *mp* 119°C)
Percentage yield ,, :

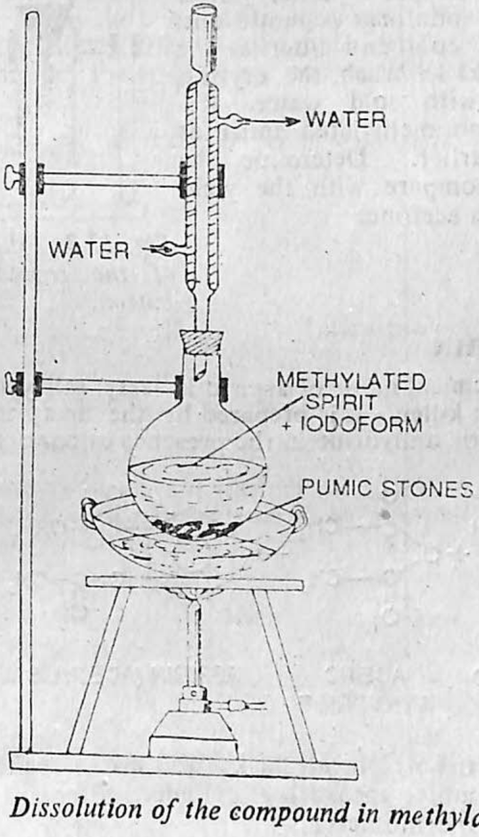


Fig. 13.2. Dissolution of the compound in methylated spirit.

Note : (*i*) If sodium hydrochloride is not available then it can be prepared from sodium carbonate and iodine.

$CH_3COCH_3+Na_2CO_3+3I_2 \rightarrow CHI_3+CH_3COONa+3NaI+H_2O+CO_2$

(*ii*) If the preparation is done on the smell scale, a boiling tube, small funnel, glass button and water pump can be used for filtration purposes (Fig. 13.3).

Iodoform from ethanol

Chemicals : Ethanol ~7 mL, sodium carbonate 15 g, and powdered iodine, 10 g.

Procedure : Take sodium carbonate and ethanol in a 250 mL beaker. Now add the powdered iodine in small amounts at a time with constant stirring. Heat the contents to 70-80°C on a water bath. After a lapse of time, yellow cyrstals of iodoform separate out. Allow it to cool and filter at the pump (Fig. 13.1). Wash the crystals thoroughly with cold water. Recrystallize from methylated spirit as suggested earlier. Determine the yield, and compare with the yield obtained with acetone.

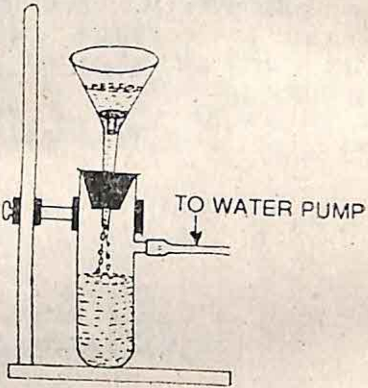
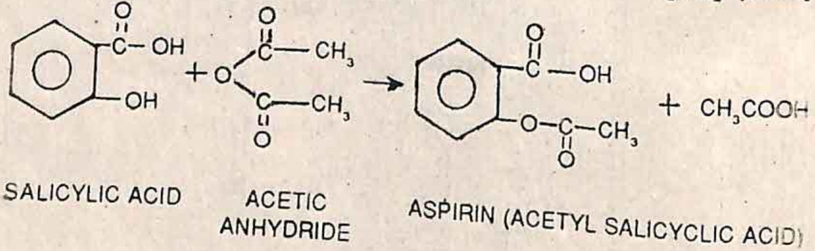


Fig. 13.3. Filtration and drying of the crystals using glass button.

13.3. ASPIRIN

The chemical name of aspirin is acetyl salicyclic acid. It is a common pain killer. It is prepared by the acetylation of salicyclic acid with acetic anhydride in the presence of conc. H_2SO_4 (catalyst).



Apparatus : Conical flasks (250 mL), beakers, water bath, filtration assembly, measuring cylinder, filter paper, glass rod, boiling tubes, thermometer.

Chemicals : Salicylic acid (5 g), acetic anhydride, 7.0 mL conc. H_2SO_4.

Procedure : In a 250 mL conical flask take 5 g salicylic acid and 7.0 mL acetic anhydride (can be taken with a measuring cylinder). Add a few drops (say 0.5 mL) of conc. H_2SO_4. Shake the reaction mixture well and heat in a water bath for 15 min. keeping the temperature about 50-60°C. Cool the contents with occasional stirring. Now pour the contents into ice cold water, ($\sim$100 mL) contained in a 250 mL beaker. Aspirin separates as white ppt. At times, vigorous stirring is essential to get the product. Filter the white mass and wash thoroughly with ice-cold water. The yield of the crude sample will be $\sim$6.0 g.

Recrystallize the crude aspirin by dissolving in 25 mL ethanol placed in a 100 mL round bottom flask fitted with a water condenser. Heat in a water bath (Fig. 13.2) to dissolve the crude mass completely. Filter the hot solution through a fluted filter paper into a 250 mL conical flask to separate any suspended impurity. Now start adding distilled water slowly until the solution assumes turidity. Heat the contents to get a clear solution. Allow the contents to cool slowly. Beautiful needle-like crystals of aspirin appear. Filter and dry the crystals on vacuum filtration assembly (Fig. 13.1).

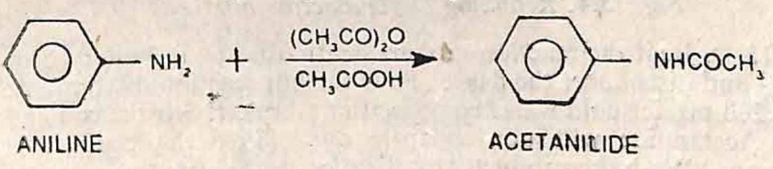
Note : Recrystallization can be done with 50% glacial acetic acid also.

Result :

Colour of the crystals :
Shape ,, ,, ,, :
Yield ,, ,, ,, : (Literature *mp* 135°C)
mp ,, ,, ,, :
Percentage yield ,, :

13.4. ACETANILIDE

Acetanilide is an important starting product for manufacturing many organic compounds. It is prepared by acetylation of aniline. Acetylation is done by using acetic anhydride and acetic acid.



ANILINE ACETANILIDE

Apparatus : Round bottom flask, measuring cylinder, beaker conical flask, air condenser, filtration assembly, filter paper, glass rod, water bath, wire gauze.

Chemicals : Aniline (redistilled or decolourised with animal charcoal), acetic anhydride, glacial acetic acid, zinc chloride, HCl, distilled water, sodium acetate.

Procedure : First Method : In a 250 mL round bottom flask, take 20 mL mixture of acetic anhydride (10 mL) and glacial acetic acid (10 mL) using a measuring cylinder. Now add 10 mL redistilled aniline slowly with stirring. Connect the flask to a reflux condenser (Fig. 13.4). Heat the reaction mixture gently for about 30 min. Stop heating and disconnect the flask. Pour the hot reaction mixture into about 200 mL ice cold water contained in a beaker. Stir the contents well. Acetanilide will soon separate out. Filter the product at the pump. Wash the product with distilled water and dry.

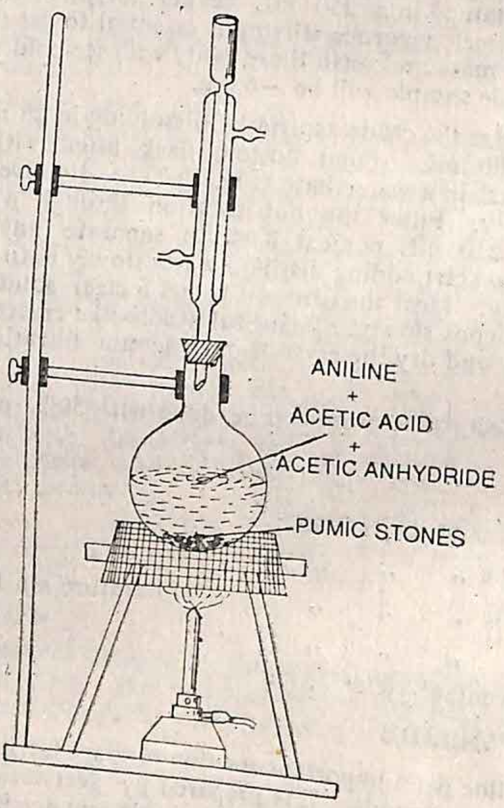


Fig. 13.4. Refluxing of the reaction mixture.

Boil the crude product with about 60 mL acetic acid (20 mL acid+40 mL water) in a beaker. Filter hot through a fluted filter paper and allow the filtrate to cool. White crystals of acetanilide separate out. Filter and wash the crystals with water and dry them on the pump. Approximate yield is ~10.0 g.

The crude product can also be recrystallized from hot water containing a little alcohol (125 mL+5 mL alcohol).

Second method : In another method of preparation, aniline (10 mL) is mixed with a 20 mL mixture of acetic anhydride (10 mL) and glacial acetic acid. About 1.2 g of $ZnCl_2$ is also added. The contents are heated in a beaker for about 1 hr. Now the hot reaction mixture is added to 200 mL ice cold water with vigorous stirring. The crude product gets separated. Filter and recrystallize. This method is quicker.

Third method : Measure out 5 mL aniline and 5 mL conc. HCl with a measuring cylinder in a 200 mL conical flask. Add ~100 mL distilled water with stirring. In a separate beaker, dissolve ~ 8.0 g of sodium acetate in ~20 mL water and add to the aniline solution. Now add ~ 6 5 mL acetic anhydride and cool the reaction vessel in an ice bath. Keep stirring the contents. After some time the solid will separate. Filter the product on the pump. Recrystallize the product from water containg a little alcohol (as saggerted earlier).

Result : Colour of the crystals ;
Shape ,, ,, :
Yield ,, ,, : (Literature *mp* 114°C)
mp ,, ,, :
Percentage yield ,, :

13.5. DIBENZAL ACETONE

Aromatic aldehydes like benzaldehyde condense with aliphatic ketones with two H-atoms linked to α-carbon atom in the presence of alkali. The condensed products are α-β unsaturated ketones.

$$C_6H_5CHO+CH_3COCH_3 \longrightarrow C_6H_5\overset{\beta}{C}H=\overset{\alpha}{C}HCOCH_3$$

However, if the two equivalents of benzaldehyde and one equivalent of acetone is made to undergo condensation reaction in the presence of sodium hydroxide, dibenzal acetone is formed.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO}+\underset{\text{Acetone}}{CH_3COCH_3}+\underset{\text{Benzaldehyde}}{OHCC_6H_5}\xrightarrow{NaOH}$$

$$\underset{\text{Dibenzal acetone}}{C_6H_5CH=CHCOCH=CHC_6H_5}+2H_2O$$

This reaction is a classical example of Claisen reaction.

Apparatus : 250 mL conical flask, filtration assembly, measuring cylinder, condenser, water bath, round bottom flask, glass rod.

Chemicals : Benzaldehyde, acetone, sodium hydroxide, methylated spirit, NaOH.

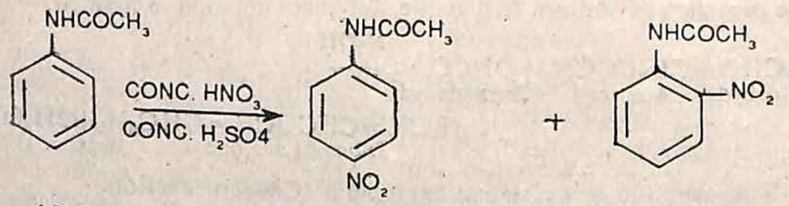
Procedure : Take 5 mL benzaldehyde, 2 mL acetone and 30 mL methylated spirit in a 250 mL conical flask. Shake the contents well by giving rotating motion to the flask. Now add 10 mL of 10% NaOH solution to the reaction mixture drop by drop with constant stirring. Cork the flask tightly and shake the contents vigorously for about 10 minutes. Release the pressure by removing and replacing the cork from time to time if necessary. Allow the contents to stand for sometime so that the reaction is complete. Cool the flask in ice bath. After sometime yellow crystals will start separating. Separate the crystals by filtering on the pump. Wash them with ice-cold water and dry. The crude product will be about ~5 g.

Recrystallize the crude product by dissolving in ~30 mL methylated spirit. Heat the contents as suggested in Fig. 13.2. Filter the hot solution through cotton plag or fluted filter paper. On cooling, the crystals of dibenzal acetone will separate. Separate the crystals by filtering on the pump. Dry the crystals by spreadings over a fold of filter paper and take the mp.

Result : Colour of the crystals :
Shape ,, ,, :
mp ,, ,, : (Literature *mp* 112°C)
Yield ,, ,, :
Percentage yield :

12.6. *p*-NITROACETANILIDE

By experience we know that the amino group is susceptible to oxidation by nitrating mixture. This makes the preparation of nitro derivative of aniline and its derivatives a difficult exercise. Under the circumstances the amino group is protected by acylation. Both the acetylamino $—CH_3\text{-}CO\text{-}NH—$ and amino groups direct the nitro group in *ortho* and *para* position. When acetanilide is nitrated, *p*-nitroacetanilide crystallizes out with a small quantity of *ortho*-derivative. The *ortho*-derivative is readily soluble in methylated spirit while the crystals of p-nitroacetanilide are not soluble The reaction is as follows :



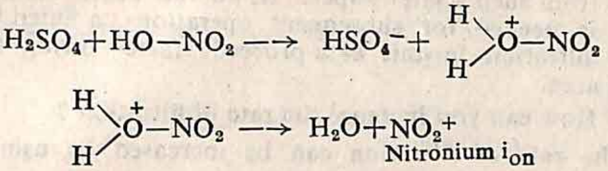
ACETANILIDE

(MAJOR)
p-NITROACETANILIDE

(MINOR)
o-NITROACETANILIDE

The nitration under the cold conditions mainly yield the para product.

Nitration of acetanilide to *p*-nitroacetanilide is a typical electrophilic substitution. The electrophile is NO_2^+ which is produced when both H_2SO_4 and HNO_3 interact.



$$H_2SO_4 + HO{-}NO_2 \longrightarrow HSO_4^- + {}^{H}_{H}\!\!>\overset{+}{O}{-}NO_2$$

$${}^{H}_{H}\!\!>\overset{+}{O}{-}NO_2 \longrightarrow H_2O + \underset{\text{Nitronium ion}}{NO_2^+}$$

Nitronium ion goes to high electron density centres, *i.e. ortho* and *para* centres present on the acetanilide molecule.

Apparatus : Conical flask, boiling tube, measuring cylinder, beaker, glass rod, water bath, thermometer.

Chemicals : Acetanilide, conc. H_2SO_4, fuming HNO_3, glacial acetic acid.

Procedure : Dissolve 10.0 g acetanilide in 10 mL glacial acetic acid contained in a 250 mL conical flask. Now add 20 mL conc. H_2SO_4 drop by drop with a dropper. Keep stirring the contents in the flask with rotating motion (the solution will become hot). Keep the reaction vessel covered with freezing mixture (salt+ice) taken in an ice bath. Note the temperature of the contents until it reaches ~5°C. Now add fuming nitric acid (4—5 mL) drop by drop to the flask placed in ice-bath, keep stirring the contents with a glass rod. Maintain the temperature ~5°C. When all the acid has been added, allow the reaction mixture to stand at room temperature for ~30 minutes. Pour the contents of the flask over crushed ice taken in a beaker, when the crude *p*-nitroacetanilide is precipitated. Stir the contents well. After a lapse of 15 minutes, separate the product by filtering on a pump. Wash the crude product well with ice cooled water and dry. The yield of the crude product is ~8 g.

Recrystallize the crude product by dissolving in ~20 mL methylated spirit as suggested under dibenzal acetone. The pure crystals of *p*-nitroacetanilide are colourless in appearance.

Result : Colour of the crystals :
Shape ,, ,, :
Yield ,, ,, :
mp ,, ,, : (Literature *mp* 214°C)
Percentage yield ,, :

Note : If the sample is too yellow. It contains the impurities of *o*-nitroacetanilide.

ORAL QUESTIONS AND ANSWERS

Q. 13.1. In what cases, are ordinary filter papers used, and in what cases, are fluted filter papers used ?

Ans. When it is desired to retain the precipitate for further operations, ordinary filter paper is used since it is easier to remove the precipitate from such a filter paper. If, on the other hand, the solution only is needed for subsequent operations, a fluted filter paper is used ; filtration in this case proceeds faster owing to a larger filtering area.

Q. 13.2. How can you increase the rate of filtration ?

Ans. The rate of filtration can be increased by using a suction pump.

Q. 13.3. Why is the filter paper made wet with water before starting the filtration ?

Ans. Water helps in the proper fixing of the filter paper against the sides of the funnel.

Q. 13.4. What is the harm if air gets in between the filter paper and the funnel ?

Ans. The rate of filtration will become slow.

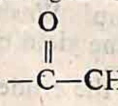
Q. 13.5. Is water always used to wet the filter paper ?

Ans. No, water is not used to wet the filter paper when the liquid to be filtered is not miscible with water

Q. 13.6. How can a liquid be transferred from a beaker to a funnel without spattering, and without running down the outer wall of the beaker ?

Ans. By pouring the solution against the stirring rod while the tip of the beaker touches the rod

Q. 13.7. What is acetylation ?



Ans. The reaction of replacing hydrogen of an hydroxyl group (—OH) or amino group (—NH_2) by $-\overset{\overset{O}{\|}}{C}-CH_2$ group is called acetylation.

Q. 13.8. Name a few acetylating agents:

Ans. Acetyl chloride (CH_3COCl) and acetic anhydride [$(CH_3CO)_2O$].

Q. 13.9. Name the acetylated products of (*i*) aniline, and (*ii*) salicylic acid.

Ans. (*i*) Acetanilide (*ii*) Acetyl salicylic acid (aspirin).

Q. 13.10. What is nitrating mixture ?

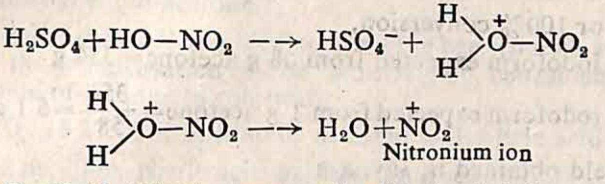
Ans. It is a mixture of conc. HNO_3 and conc. H_2SO_4.

Q. 13.11. What is nitration ?

Ans. The replacement of hydrogen in an organic compound by nitro-group is called nitration.

Q. 13.12. What is nitronium ion ? How is it obtained ?

Ans.



$$H_2SO_4+HO{-}NO_2 \longrightarrow HSO_4^-+ \begin{array}{l}H\diagdown\\ \quad\;\; \overset{+}{O}{-}NO_2\\ H\diagup\end{array}$$

$$\begin{array}{l}H\diagdown\\ \quad\;\; \overset{+}{O}{-}NO_2\\ H\diagup\end{array} \longrightarrow H_2O+\underset{\text{Nitronium ion}}{\overset{+}{N}O_2}$$

Q. 13.13. Which compounds will give iodoform reaction ?

Ans. Compounds that contain the CH_3CO—group and which can be oxidized by iodine to CH_3CO—group give iodoform reaction.

Q 13.14. What happens when aniline is treated with nitrating mixture ?

Ans. It is oxidized to benzoquinone.

Q. 13.15. Nitration of acetanilide by nitrating mixture gives a mixture of both *ortho* and *para* nitroacetanilide. Suggest a method of decreasing the percentage of *ortho*-nitroacetanilide in the nitration reaction.

Ans. The percentage of *ortho*-nitroproduct decreases when the nitration reaction is carried out at low temperature.

Q 13.16. Name the condensation product formed when acetone and benzaldehyde are taken in equimolar ratio in the preparation of dibenzal acetone.

Ans Benzylidene acetone will be formed.

$$C_6H_5CHO+CH_3COCH_3 \xrightarrow{\text{NaOH}} \underset{\text{Benzylidene acetone}}{C_6H_5CH{=}CHCOCH_3}$$

Q. 13.17. How is ethanol converted into iodoform ?

Ans. Ethanol is first oxidized to acetaldehyde by hypohalite which, in turn, is iodinated by iodine in the presence of a base to yield tri-iodomethane or iodoform.

$$C_2H_5OH \xrightarrow{\text{Oxidation}} CH_3CHO$$

$$CH_3CHO \xrightarrow{NaOH/I_2} Cl_3CHO \xrightarrow[H{-}CO_2H]{\text{Hydrolysis}} \underset{\text{Iodoform}}{CHI_3}$$

Q. 13.18. Give the common uses of iodoform and aspirin.

Ans. Iodoform is used as a common disinfectant.

Aspirin is a popular pain-killer.

Q. 13.19. How will you calculate the theoretical yield of iodoform when acetone is the starting material ?

Ans. For calculating the theoretical yield,

Molecular mass of acetone $CH_3COCH_3=58$

Molecular mass of iodoform $CHI_3=394$

Hence, for 100% conversion,

Mass of iodoform expected from 58 g acetone$=354$ g

Mass of iodoform expected from 1 g acetone$=\frac{354}{58}=6.1$ g

If the yield obtained is, say, x g

Percentage yield obtained$=\frac{x}{6.1}\times 100\%$

Q. 13.20. Acetylation of phenol is not done conveniently in alkaline medium using acetyl chloride. Comment.

Ans. In alkaline medium, acetyl chloride hydrolyses rapidly to acetic acid.

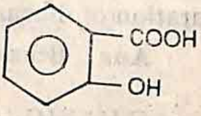
Q. 13.21. Suggest a method of carrying out the acetylation of phenols.

Ans. Acetylation of phenols can be carried out by using acetic anhydride in the presence of conc. sulphuric acid as a catalyst :

$$C_6H_5OH+(CH_3CO)_2O \xrightarrow{H_2SO_4} C_6H_5OCOCH_9+CH_3CO_2H$$

Q. 13.22. What is salicylic acid ?

Ans. Salicylic is *o*-hydroxybenzoic acid.



Q. 13.23. Aniline sample is usually yellowish brown in colour. Comment.

Ans. Pure aniline is a yellowish brown coloured liquid. When exposed to light and air and kept for long it gets oxidized to peroxo compounds and assumes yellowish brown colour.

Q. 13.24. Why do we add some methylated spirit to water during crystallization of acetanilide ?

Ans. In aqueous solution, solubility of acetanilide depends upon temperature. In cold solution it gets separated quickly. As a result, good crystals are not obtained. Addition of rectified spirit or methylated spirit to the solution increases the solubility of acetanilide. On slow precipitation, crystals of big size are obtained.

Q. 13.25. What is Claisen reaction ?

Ans. It is the condensation reaction of two equivalents of benzaldehyde with one equivalent of acetone in the presence of aqueous sodium hydroxide to dibenzal acetone.

Q. 13.26. Why do we add alcohol to the reaction mixture of benzaldehyde and acetone ?

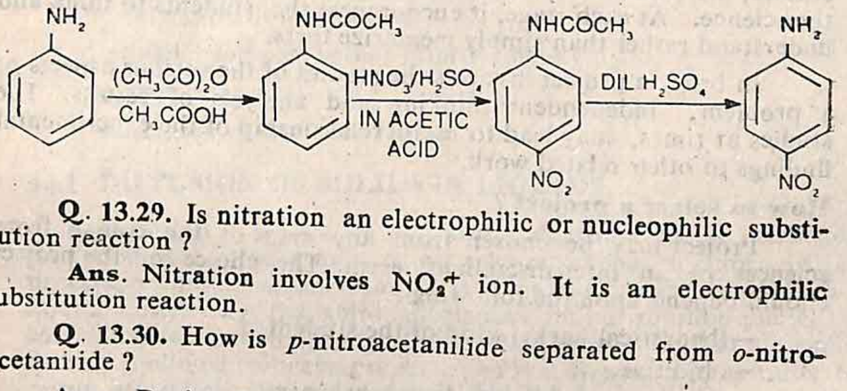
Ans. Alcohol is added to keep the benzylidene acetone, formed by the condensation of one molecule of benzaldehyde with one molecule of acetone in solution.

Q. 13 27. Can aniline be nitrated with nitric acid ?

Ans. No. Nitric acid oxidizes aniline.

Q. 13.28. How is nitroaniline prepared ?

Ans. Nitroaniline is prepared by first protecting the amino group by acetylation. Acetylamide group is *ortho* and *para* directing group. This group is later hydrolysed to amino group after nitration.



Q. 13.29. Is nitration an electrophilic or nucleophilic substitution reaction ?

Ans. Nitration involves NO_2^+ ion. It is an electrophilic substitution reaction.

Q. 13.30. How is *p*-nitroacetanilide separated from *o*-nitroacetanilide ?

Ans. During the course of crystallization *o*-nitroacetanilide remains in ethanol as it is more soluble in ethanol.

Q. 13.31. At times the sample of *p*-nitroacetanilide appears yellow. Comment.

Ans. It is due to the presence of impurities. Along with *p*-nitroacetanilide, a small amount of *o*-nitroacetanilide is also formed which is yellow in colour.

□ □

UNIT 14

Investigatory Projects

It is always interesting to learn through visual experiments and activities. Investigatory project is a step only in that direction. It involves the investigation of a problem through scientific knowledge and its application. A project work differs from routine class experiments since it necessarily makes investigation a single theme through a series of related experiments. The project studies can always be made exciting by keeping its ends open. Through such studies, the students understand the significance and relevance of the science. At each stage, it encourages the students to think and understand rather than simply memorize facts.

In brief, a project involves the studies of the various aspects of a problem, independent thinking and analysis of results. The studies at times, may lead to useful relationship of the experimental findings to other related work.

How to select a project ?

Project may be chosen from any area of the course from sciences or an inter-disciplinary area. The choice of the project should depend upon the following :

—theoretical background of the student
—objective......
—competence of the student, teacher, etc.
—facilities available in the school and at home
—accessibility to the other places where facilities are available
—interests, inquisitiveness and efforts of the students
—motivation
—self confidence and determination.

Working of the project

Some of the relevant points are listed below :

—planning, collection of information, keeping in view the object, collection of apparatus and chemicals.
—execution of the plan and experiments

- —proper recording of the results
- —rechecking of the results
- —interpretation of the results
- —applications, etc.

Presentation of the project

The general lay out for recording the project is suggested below :

- —title of the project
- —general introduction
- —required materials'
- —detailed experimental procedure
- —experimental observations
- —discussions and conclusions
- —interpretation of results
- —suggestion for further improvement
- —applications
- —bibliography

14.1. DIFFUSION OF SOLIDS IN LIQUIDS

Diffusion of a solid in liquid is understood as the dispersion of a solid in the liquid so as to get a homogeneous mixture. In the process, a phase change occurs, as it does when a gas dissolves in a liquid, converting the solid substances into a solution phase. A solution of a solid solute in a liquid has properties that are significantly modified from the properties of the liquid. For solution to occur, attraction between solvent and solute particles must take place. As the solution process occurs (Fig. 14.1) particles are pulled away from the crystal lattice by the attraction of the solvent molecules. When sugar dissolves in water, the hydrogen bonds between the C—OH groups of the sugar molecules in the crystalline solid are replaced by hydrogen bonds between these C—OH groups and water molecules. When iodine dissolves in CCl_4, the van der Waals forces between iodine molecules in the solid are replaced by the van der Waals forces between iodine and CCl_4 molecules. If the attraction between solid particles or between liquid particles is greater than the attraction between solid and liquid, solution process will not take place. To some extent this solvent-solute attraction reduces the freedom of the solvent molecules.

The dispersion of the solid in liquid will thus depend upon the nature of solid and liquid, external conditions, etc. The solution process is generally endothermic:

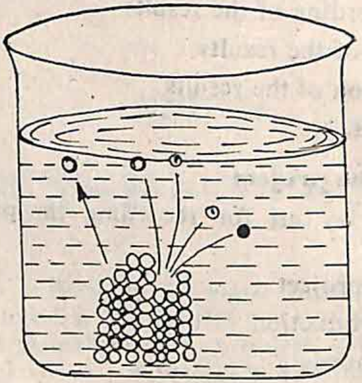


Fig. 14.1. A solid solute dissolves by solute particles leaving the solid phase and becoming distributed in the solution phase.

Experiment 14.1. 1. To study the rates of diffusion of potassium dichromate and copper sulphate in water.

General : When potassium dichromate diffuses in water, the solution assumes orange colour. And the solution of copper sulphate assumes blue colour. Hence diffusion of coloured solids in water can be visualized by the dispersion of the respective colour in water. Quick dispersion of a colour of a solid exhibits the higher rate of its diffusion in water.

Apparatus : Two 250 mL graduated measuring cylinders, two stop watches.

Chemicals : Potassium dichromate, copper sulphate, distilled water.

Procedure. Take a fixed volume say 150 mL of distilled water in the graduated cylinders marked as I and II. Place a crystal of copper sulphate (~2g in mass) gently at the bottom of cylinder I. Start the stop watch and note the height of the crystal in the cylinder to get the initial stage of diffusion. Now place a crystal of potassium dichromate of mass ~2g in the second cylinder II. Start the stop watch and note the initial stage as with copper sulphate. Note the rise in the height of the coloured solutions at different intervals of time and also the time taken by each colour to reach the desired volume mark in both the cylinders. You would notice that it is different in both the cases. This shows that the rate of diffusion of different solutes in water is different. Plot a graph between the height of the coloured solution against the time, taking time along X-axis and height along Y-axis (Fig. 14.2).

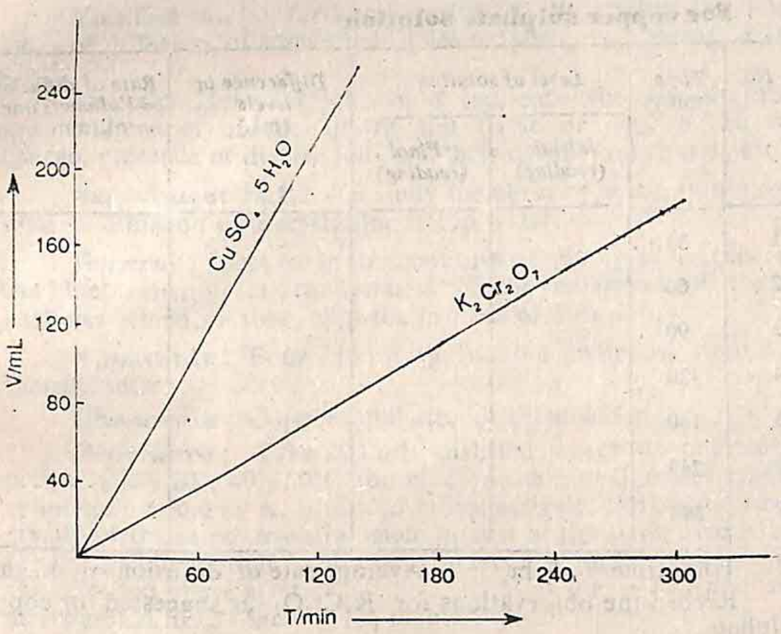


Fig. 14.2. Graph of height of the column of coloured solution against time.

Observations :

Room temperature= ...°C

Mass of $CuSO_4.5H_2O$ crystal=...g

Mass of $K_2Cr_2O_7$ crystal=...g

Molecular mass of $CuSO_4.5H_2O$=249.5 g/mol

Molecular mass of $K_2Cr_2O_7$=294 g/mol

Molecular mass of Cu^{2+} ion=63.5 g/mol

Molecular mass of $Cr_2O_7^{2-}$ ion=216 g/mol

For copper sulphate solution

S. No.	*Time* (min)	*Level of solution*		*Difference in levels* (mL)	*Rate of diffusion* =*Volume/Time* =mL/min
		Initial (reading)	*Final (reading)*		
1	30				
2	60				
3	90				
4	120				
5	180				
6	240				
7	300				

Total time=...5 hr   Average rate of diffusion=...mL/min

Record the observations for $K_2Cr_2O_7$ as suggested for copper sulphate.

Results and Discussion

Both from the observations at constant temperature and graph, it can be inferred that copper sulphate diffuses at a faster rate than potassium dichromate.

Diffusion, as understood experimentally by the movement of coloured boundary upward, is in fact diffusion of coloured ions (Cu^{2+} and $Cr_2O_7^{2-}$) upwards.

Despite the amount of the salts and the same experimental temperature, there is a difference in the rate of diffusion. Under the circumstances, the rate of diffusion appears to be related to the molecular masses of the dispersing coloured ions, i.e. Cu^{2+} and $Cr_2O_7^{2-}$.

According to Graham's law of diffusion, rates of diffusion of gases are inversely proportional to the square roots of their molecular masses. If this law were true in the case of diffusion of ions, relative rates of diffusion of $Cr_2O_7^{2-}$ and Cu^{2+} should be

$$=\sqrt{\frac{63.5}{216}}=\frac{1}{\sqrt{3.4}}=\frac{1}{1.84}$$

that is, Cu^{2+} ions should diffuse 1.84 times more rapidly than $Cr_2O_7^{2-}$ ions.

Actual ratio between their rates of diffusion as found experimentally is...... This is in agreement to the expected ratio.

This fact can be further investigated by noting the relative rates of diffusion of some other coloured ions, e.g., MnO_4^-, CrO_4^{2-}, Co^{2+}, etc.

The other factors which could influence the rate of diffusion are : nature of charge on the ion (+ve or -ve), magnitude of charge, presence of diverse ions and their nature and charge, etc.

Experiment 14.1.2. To study the effect of temperature on the rates of diffusion of a crystalline salt in water.

General : Increase in temperature or supply of heat increases the kinetic energy, i.e., randomness of the molecules of the solid particles which, in turn, help the process of diffusion.

Apparatus : Four 250 mL graduated cylindes, stop watch, thermometer.

Chemicals : Copper sulphate, distilled water.

Procedure : Take 200 mL distilled water at different temperature, say 20°, 40°, 50°C and 60°C in the four different graduated cylinders marked as A, B, C and D respectively. Put copper sulphate crystal of the same mass in each almost at the same time. Observe the rise of blue colour in all the cylinders. Note the rise in level of the coloured phase after every half an hour for ~3 hr and record as suggested in the table given below :

Observations :

Mass of copper sulphate added to each solution : ~5 g

Volume of water in each cylinder : 200 mL

Cylinder	*Temperature*	*Level of coloured phase of different intervals of time*					
		30 min	*60* min	*90* min	*120* min	*150* min	*180* min
A	20°C	......mL	......mL	......mL	......mL	......mL	......mL
B	40°C	......mL	......mL	......mL	......mL	......mL	......mL
C	50°C	......mL	......mL	......mL	......mL	......mL	......mL
D	60°C	......mL	......mL	......mL	......mL	......mL	......mL

Results and Discussion

It is seen from the table that rate of diffusion of solid molecules increases with increase in temperature. One can say that the velocity of an ion increases with rise in temperature. Hence, the rate of diffusion, which depends on the velocity of ions, increases with rise of temperature.

If we perform the experiment with water at ten different temperatures, we shall have rate of diffusion at ten different temperatures. A graph can be planned between temperature and rate of diffusion. From the shape of the curve one can inferred the relation between temperature and the rate of diffusion.

Note : A few more experiments can be planned say,

—the effect of size of the crystals on the rate of diffusion

—the effect of charge carried by the ion on the rate of diffusion.

—etc.

QUESTIONS

1. What is meant by the term diffusion ?
2. State the Graham's law of diffusion of gases.
3. Why do substances diffuse into liquids ?
4. How does diffusion of a solid in a liquid take place ?
5. State the factors which affect the diffusion of a solid in a liquid.

14.2. ROLE OF MANGANESE DIOXIDE IN THE PREPARATION OF OXYGEN GAS.

Many reactions proceed quite slowly when the reactants are mixed alone but can be made to occur much more rapidly by adding some other substance. Such substances are called **catalysts** which alter the rate of a chemical reaction without experiencing any significant change. In the preparation of oxygen from potassium chlorate, mangance dioxide is used as a catalyst.

Generally a catalyst is used to speed up a reaction but there are also catalysts that slow down a reaction. A substance of this type is sometimes called a negative catalyst or an inhibitor. A catalyst alters the speed of the reaction by changing the activation energy or the energy barrier. Figure 14.3 shows how a catalyst that speeds up a reaction works by decreasing the activation energy, while a negative catalyst increases the activation energy.

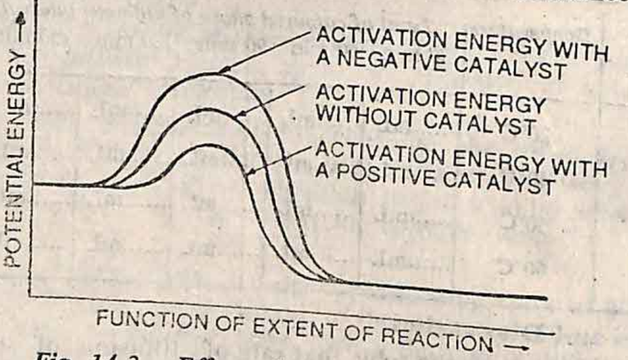


Fig. 14.3. Effect of a catalyst on the activation energy of a reaction.

You have already read about the mechanism of catalysis in your theory classes. (Unit 6 class XII text book).

(*i*) Catalyst does not experience any chemical change.

(*ii*) Effectiveness of a catalyst depends upon its active surface area (catalysis is a surface phenomenon).

(*iii*) The rate of reaction is affected by the amount of catalyst.

(*iv*) Catalysts are selective in nature *i.e.* same catalyst cannot be employed for every reaction.

Some of the properties can be investigated experimentally by designing simple experiments.

14.2.1. To determine the minimum quantity of manganese dioxide required for the preparation of oxygen gas.

General : In the laboratory, oxygen is prepared by heating potassium chlorate in the presence of manganese dioxide, which acts as a catalyst.

$$2KClO_3 \xrightarrow[\text{Heat}]{MnO_2} 2KCl+3O_2$$

To ascertain the minimum quantity of manganese dioxide which is just sufficient for the decomposition of potassium chlorate it is desired to take a number of mixtures of potassium chlorate and manganese dioxide in which the quantity of potassium chlorate is fixed whereas the quantity of manganese dioxide is varied. The rate of the evolution of oxygen gas in each case is determined. From the rate one can find the mixture from which oxygen is evolved at the highest rate.

Apparatus : Fifteen hard glass test tubes, corks, delivery tube, beehive shelf, graduated tube or cylinder and stop watch.

Chemicals : Potassium chlorate, manganese dioxide and water.

Procedure : Take 15 hard glass test tubes. Clean and label them from 1 to 15.

Take 5 g potassium chlorate in each. Then take manganese dioxide in each test tube in the following proportions :

Test tube	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
$KClO_3$, g	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
MnO_2, g	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0

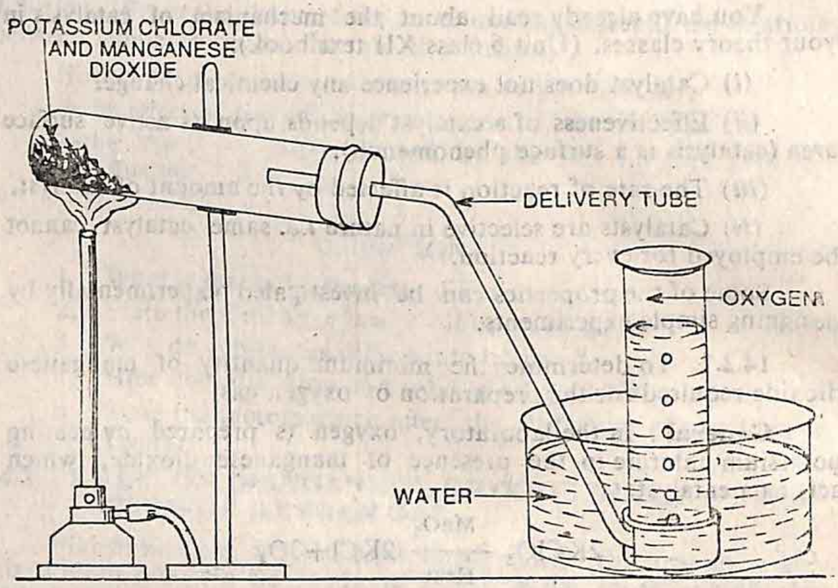


Fig. 14.4. Preparation of oxygen

Set up the apparatus for the preparation of oxygen gas as shown in Fig. 14.4. Clamp hard glass test-tube no. 1 with its mouth tilted slightly downward.

Now heat the test tube and allow a few bubbles of oxygen to escape and then place a graduated tube or cylinder filled with water over the beehive shelf and immediately start the stop watch. Note the time when water level in the tube or cylinder is at 10.0 mL (i.e., 10 mL of oxygen is collected in the tube). Suppose this time is t_1 s.

Repeat the experiment with tubes 2, 3, ... and 15. Let the time be t_2, t_3......and t_{15}. Record the observations as suggested below :

Observations :

Mass of $KClO_3$ taken each time=5 g

Mass of MnO_2 taken from 0.2—0.3 g as suggested earlier.

Tube	*Volume of oxygen collected*	*Time taken in minutes*	*Rate of decomposition =Volume of O_2 evolved per minute*
1	10 mL	t_1	$5/t_1=$
2	,,	t_2	$5/t_2=$
3	,,	t_3	$5/t_3=$
4	,,	t_4	$5/t_4=$
5	,,	t_5	$5/t_5=$
6	,,	t_6	$5/t_6=$
7	,,	t_7	$5/t_7=$
8	,,	t_8	$5/t_8=$
9	,,	t_9	$5/t_9=$
10	,,	t_{10}	$5/t_{10}=$
11	,,	t_{11}	$5/t_{11}=$
12	,,	t_{12}	$5/t_{12}=$
13	,,	t_{13}	$5/t_{13}=$
14	,,	t_{14}	$5/t_{14}=$
15	,,	t_{15}	$5/t_{15}=$

Result : The minimum amount of MnO_2 required for decomposing 5 g of $KClO_3$ is....... Also calculate the amount of MnO_2 required for 100 g of $KClO_3$, i.e. 9% MnO_2 required.

Conclusion. For maximum yield of oxygen, percentage of MnO_2 in the mixture of $KClO_3$ and MnO_2 should be about 21.9%. It is for this reason the mixture of $KClO_3$ and MnO_2 is taken in the ratio of 4 : 1 for the preparation of oxygen in the laboratory.

Precautions : (*i*) MnO_2 should be free from carbon. In the presence of carbon explosion may take place on heating due to fast oxidation of carbon by $KClO_3$.

(*ii*) The test tube should be placed with its mouth sloping down so that any moisture if condensed does not move to the hot part of the test-tube. This will prevent the breaking of tube.

(*iii*) The tube should be heated gradually so that the evolution of oxygen can be controlled.

(*iv*) The delivery tube should be removed from the water trough before stopping the heating of the tube to prevent back suction.

Note : Oxygen gas can also be prepared by decomposition of hydrogen peroxide. Manganese dioxide also acts as a catalyst for the decomposition of hydrogen peroxide. No heating is required in this method.

$$2H_2O_2 \xrightarrow{MnO_2} 2H_2O + O_2$$

QUESTIONS

1. What is the role of MnO_2 for the preparation of oxygen gas ?

2. What is a catalyst ? How does it work ?

3. Mention some characteristics of a catalyst which affect its functioning.

4. Do all catalysts always accelerate the rate of chemical reactions ? Comment.

5. What are negative and positive catalysts ?

6. Which of the two substances is preferred to prepare oxygen and why ? (*i*) $KClO_3$ and (*ii*) H_2O_2.

14.3. ORDER OF A REACTION

The rate of a chemical reaction depends upon the concentration of the reactants and it alters as the reaction proceeds.

The number of reacting molecules whose concentration alters as a result of chemical change is called the "Order of reaction".

For a general reaction

$$mA + nB \rightarrow pC + \ldots\ldots$$

Consider that the concentration of the reactants A and B alters during the reaction.

At any instant, the rate $\left|\frac{dx}{dt}\right|$ will, therefore, be given by the equation :

$$\frac{dx}{dt} = k\,[A]^m\,[B]^n$$

and the order of the reaction will be $(m+n)$.

where k is the rate constant. Here the exponents m and n are called the **order of reaction** with respect to A and B respectively. The sum $(m+n)$ is known as **overall order** of the reaction. The following points concerning the order of a reaction be carefully noted :

1. **The order of a reaction with respect to different reactants has to be obtained experimentally by determining the rate law.**
2. **The order of reactions are frequently whole numbers but it can also have \fractional values,** e.g. **0, 1, 2, 3,** 3/2, 1/2, etc.
3. **The order of a forward reaction is always positive. However, for a reversible reaction, the order can have negative value also.**
4. **The order of a reaction is an experimentally determinable quantity. It cannot be predicted theoretically on the basis of stoichiometry of the reaction.**
5. **A reaction may proceed in several steps, the overall order of a reaction is calculated by the rate determining step.**

Thus a reaction may be zero, first, second or third order according as the value of $(m+n)$ comes out to be zero, one, two or three respectively.

Consider a simple reaction :

$$\begin{array}{ll} A \longrightarrow & B \\ a & 0 \ldots \text{Initial concentration} \\ a-x & x \cdots \text{After time } t \end{array}$$

Let us start with a g mol of reactant A and let x g. mol undergo change in time interval t, then

$$\text{Rate of reaction, } \frac{dx}{dt} \propto (a-x)$$

or,

$$\frac{dx}{dt} = k\,(a-x)$$

where k is rate constant or velocity coefficient or specific reaction rate.

Experiment 14.3.1. To determine the rate constant of the hydrolysis of methyl acetate catalysed by 0.5 N-HCl.

Apparatus : A constant temperature bath, conical flask, burette, pipette, stop watch, etc.

Chemicals : Methyl acetate, HCl, NaOH, phenolphthalein, ice, water.

Procedure : Take methyl acetate and 0.5 N—HCl in separate bottles and keep them in a theromstat for half an hour. When they assume the temperature of the bath, mix 5 mL of methyl acetate and 100 mL of 0.5 N—HCl. Immediately withdraw 5 mL of the reaction mixture with the help of a pipette and pour into a

250 mL conical flask containing ice pieces (made of distilled water) to quench the reaction. Now titrate the solution by adding N/50 solution of a NaOH from the burette using phenolphthalein as an indicator. Similarly again, pipette out 5 mL of the reaction mixture after five minutes and repeat the procedure. Repeat the above procedure by withdrawing 5 mL of the reaction mixture after 10, 15, 20, 30, 45 minutes. These titre readings give the value of V_t at different intervals of time. The V_∞ reading corresponds to the reading when hydrolysis is complete. To obtain this reading, at times the remaining mixture is titrated after 20 hr. But generally it is advisable to heat the mixture at ~50°C for about an hour to complete the reaction and then V_∞ is determined by titrating with NaOH.

Observations :

t (min)	Volume of alkali i.e. V_t (mL)	$V_\infty - V_t = (a-x)$	$\log (a-x)$	$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$ (min^{-1})
0	V_0	$V_\infty - V_0 = a$	—	—
10	V_{10}	$V_\infty - V_{10}$	—	—
15	V_{15}	$V_\infty - V_{15}$	—	—
20	V_{20}	$V_\infty - V_{20}$	—	—
30	V_{30}	$V_\infty - V_{30}$	—	—
45	V_{45}	$V_\infty - V_{45}$	—	—
∞	V_∞	—	—	—

Calculations :

$$V_\infty - V_0 = a$$

$$V_\infty - V_t = (a-x)$$

$$\therefore \qquad k = \frac{2.303}{t} \log_{10} \frac{V_\infty - V_0}{V_\infty - V_t}$$

Result : If the values of k are constant then the hydrolysis of CH_3COOCH_3 is a first order reaction.

On plotting a graph between $\log \frac{V_\infty - V_0}{V_\infty - V_t}$ and t, a straight line passing through the origin is obtained. The slope gives the rate constant for the reaction.

The rate of reaction can be calculated from the equation

$$\frac{dx}{dt}=k(a-x)$$

Precautions : (*i*) The reactants are allowed to attain the temperature of the thermostat or water bath.

(*ii*) The zero time should only be noted when ice is added to the first 5 mL of the reaction mixture.

(*iii*) Titrations should be performed immediately when aliquot has been taken out.

Experiment 14.3.2. To determine the rate constant of the saponification of ethyl acetate using sodium hydroxide.

Apparatus : As suggested in Experiment 14.3.1.

Chemicals : Ethyl acetate, NaOH, HCl or H_2SO_4.

Hint : The hydrolysis of ethyl acetate by sodium hydroxide is given by the equation

$$CH_3COOC_2H_5+NaOH \longrightarrow CH_3COONa+C_2H_5OH$$

To study this reaction, equimolecular quantities of ethyl acetate and sodium hydroxide are mixed together and 5 mL of the mixture is withdrawn at regular intervals of time and then titrated against standard HCl or H_2SO_4 solution. The amount of acid used will correspond to unused alkali, i.e. $(a-x)$. The initial concentration a of the alkali will correspond to the volume of acid used initially.

These experimental values of a and $(a-x)$ are then substituted in rate equations for first, second and third order reactions and the value of k is calculated. The equation which gives the constant value of k will determine the order of reaction. The results in this case show that hydrolysis of ethyl acetate is a reaction of the second order since the value of k comes constant when the following equation is used

$$k=\frac{1}{l}\cdot\frac{x}{a(a-x)}$$

Knowing the value of k and $(a-x)$ at any instant the rate of hydrolysis can be determined by the following equation

$$\frac{dx}{dt}=k(a-x)(a-x)$$

Here k is velocity constant, a the initial concentration of reactants and x is the amount of ethyl acetate hydrolysed or alkali used at any time t.

QUESTIONS

1. Define rate of a reaction. How does the concentration of reactants affect the rate of a reaction ?

2. Explain the differences between order and molecularity of a reaction.

3. List the important factors which affect the rate of a reaction.

4. Distinguish between rate and rate constant. Give units of rate constant.

5. What is saponification ?

6. What is quenching ?

14.4. ADSORPTION

Surfaces of both liquids and solids, unlike their bulk are constantly under the influence of unbalanced attractive forces. These unbalanced forces are called residual valence forces. Solids in particular are endowed with unbalanced forces at their surfaces by the incomplete valence bonds.

As a result, solid surfaces tend to satisfy their residual forces by attracting and retaining on them the molecules of other substances which come in their contact. As the molecules remain only at the surface and do not penetrate into the bulk, their concentration is more at the surface than in the bulk of the solid. The phenomenon of higher concentration of any substance on the surface than in the bulk of a solid is called **adsorption** (Fig. 14.5). Thus adsorption refers to the relatively higher concentration of the adsorbed material (adsorbate) on the surface of the adsorbent (solid) as compared to its concentration in the bulk phase (of the absorbed material).

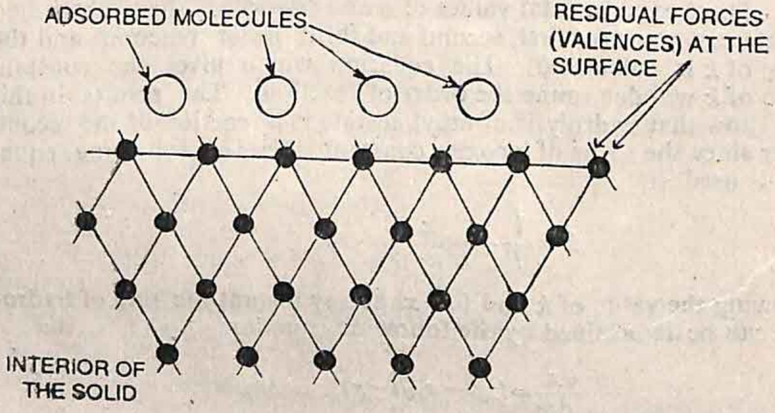


Fig. 14.5. Adsorption on the surface of a solid by residual forces (valences).

The amount of the substance adsorbed is proportional to the concentration of the solution and is given by the relationship (**Freundlich adsorption Isotherm**).

$$\frac{x}{m}=kc^{1/n}$$

where x=Amount of solute adsorbed

m=Amount of adsorbent

k=A constant depending upon the nature of both adsorbent and adsorbate.

c=Equilibrium concentration of adsorbate in the solution.

n=A constant depending upon the nature of the adsorbate.

The value of $1/n$ is generally less than unity. Taking logarithms of the equation, we get

$$\log \frac{x}{m}=\log k+\frac{1}{n}\log c$$

If the values of $\log \frac{x}{m}$ are plotted as ordinate against $\log c$ as abscissa, we get a straight line (Fig. 14.6), with a slope $1/k$ and intercept on the ordinate $\log k$.

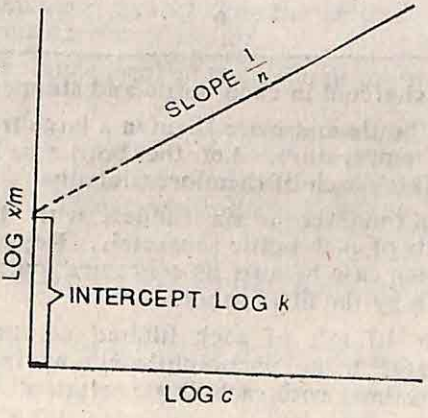


Fig. 14.6. Freundlich adsorption isotherm. A plot between $\log \frac{x}{m}$ *and* $\log c$.

Experiment 14.4.1. To study the adsorption of acetic acid on charcoal and prove the validity of Freundlich's adsorption isotherm.

Apparatus : Six stoppered reagent bottles, 2 burettes, pipette, measuring cylinder, funnels, trough, measuring flasks.

Chemicals : Acetic acid, sodium hydroxide, powdered activated charcool, phenolphthalein.

Procedure : Prepare standard stock solution of each acetic acid (0.5 M) and sodium hydroxide (1.0 M).

Take 6 neat and dry stoppered reagent bottles. Label them from 1 to 6.

Set up two burettes. Fill one with 0.5 M acetic acid and the other with distilled water.

Add the solutions to bottles as suggested below :

Bottle No.	*Vol. of 0.5* M CH_3COOH (mL)	*Vol. of water* (mL)
1	50	0
2	40	10
3	30	20
4	20	30
5	10	40
6	0	50

Add 4 g of charcoal in each bottle and stopper them.

Shake each bottle and place them in a large trough containing water at room temperature. Let the bottles be in the trough for about 45 min shaking each of them occasionally.

In the mean time, set up six funnels with dry filter papers. Filter the contents of each bottle separately. Reject first 4-5 mL of the solution in each case because its concentration might be affected due to adsorption by the filter paper.

Pipette out 10 mL of each filtered solution and titrate it against 0·1 M NaOH using phenolphthalein as indicator. Repeat the titration three times with each bottle solution.

Observations :

Mass (m) of the activated charcoal in each bottle=4 g

Temperature of water =...°C

Bottle No.	Vol. (in ml) of 0.1 M NaOH used for 10 ml of filtered solution after adsorption	Initial concentration (mol/L) of acetic acid, c_1	Equilibrium concentration (mol/L) of acetic acid after adsorption, c	Amount (in moles) of acetic acid adsorbed $x = \frac{(c_1 - c) \times 50}{1000}$	x/m	$\log \frac{x}{m}$	$\log c$
1		$\frac{0.5 \times 50}{50}$					
2		$\frac{0.5 \times 40}{50}$					
3		$\frac{0.5 \times 30}{50}$					
4		$\frac{0.5 \times 20}{50}$					
5		$\frac{0.5 \times 10}{50}$					
6		—					

Calculations :

(*i*) Calculate c_1 by including the dilution factor as given in the third column above.

(*ii*) Calculate c (mol/L) from the titration data.

(*iii*) Plot log $\frac{x}{m}$ values (ordinate) versus log c (abcissa).

Result : The plot is a straight line which shows the validity of the Freundlich adsorption isotherm over the concentration range studied.

Precautions : (*i*) The bottles should be absolutely dry and clean.

(*ii*) NaOH used should be free from CO_2.

(*iii*) For filtration, small filter papers should be used so that error due to any adsorption of the acid by the filter paper is minimized.

Following exercises can also be planned :

1. To study the adsorption of oxalic acid solution on charcoal and verify the Freundlich adsorption isotherm.

2. To determine the adsorption isotherm of iodine from its alcoholic solution by activated charcoal. Use $Na_2S_2O_3$ solution and starch (indicator) for titrating unadsorbed iodine.

3. To study the adsorption isotherm of benzoic acid on active charcoal.

QUESTIONS

1. What is adsorption ?

2. State the difference between absorption and adsorption.

3. Explain the following :

(*i*) Surfaces of both liquids and solids are under the influence of unbalanced forces.

(*ii*) The process of adsorption is faster than the absorption process.

(*iii*) The extent of adsorption depends upon the surface area of adsorbent.

4. Differentiate between in each of the following sets :

(*a*) Adsorbent and adsorbate.

(*b*) Chemisorption and physisorption.

5. (*a*) Suggest the probable mechanism of adsorption.

(*b*) List the various factors which govern the degree of adsorption of liquids on solids.

6. Explain the two terms—adsorption isotherms and adsorption isobars. Describe Freundlich's adsorption equation.

7. How does the extent of adsorption vary with temperature and pressure ? Explain.

8. Write short notes on :

(*a*) Catalytic reaction and adsorption, and

(*b*) Adsorption from solutions.

9. Explain why adsorption is usually accompanied be decrease in enthalpy ? Why does adsorption stop after some time ?

14.5. HARDNESS OF WATER

Water which does not easily produce lather with soap is known as **hard water**. All natural waters contain small quantities of dissolved salts which vary greatly in composition from one area to another. Dissolved salts of Ca^{2+} and Mg^{2+} contribute to hardness in ground water. These are found associated with bicarbonate, chloride and sulphate ions. A soap such as sodium octadecanoate, $C_{17}H_{35}COONa$ reacts with Ca^{2+} and Mg^{2+} ions to form an insoluble scum of calcium and magnesium octadecanoate.

Hardness of water presents many problems in the use of water. Some of these are :

(*i*) Scale formation on heating surfaces in boilers and cooling water equipments.

(*ii*) In cleaning processes, soaps, before forming lather, react first with salts in waters to form insoluble calcium and magnesium stearates and oleates which form not only objectionable precipitates but also result in more consumption of soaps in producing lathering properties of water since no lather can be obtained with the soap until all the 'hardness' has been reacted.

Hardness of water is of two types :

1. Temporary hardness, and
2. Permanent hardness.

Experiment 14.5.1. To determine the total hardness in the given sample of water.

General : The hardness of water is due to dissolved salts of calcium and magnesium. Hardness is of two kinds—temporary and permanent. Temporary hardness is due to bicarbonates of calcium and magnesium and can be removed by boiling. Permanent hardness is due to sulphates and chlorides of calcium and magnesium and is not removed by boiling.

Hardness of water is expressed in terms of calcium carbonate equivalent to the amount of different soluble salts and can be determined by titration with standard acid.

Apparatus : Conical flask, porcelain dish, measuring cylinder, pipette 100 mL, pipette 25 mL, burette, funnel.

Chemicals : Sulphuric acid, sodium carbonate solution, sodium hydroxide, methyl red indicator.

Procedure : Prepare the following solutions :

Sulphuric acid : 0.1 N and 0.02 N

Sodium carbonate : 0.1 N

Sodium hydroxide : 0.1 N.

A. Esiimation of temporary hardness

Take 100 mL of filtered water in a 500 mL conical flask with a 100 mL pipette or 100 mL measuring flask. Add a few drops of methyl red indicator. Now run the N/50 sulphuric acid solution from the burette until the solution of the colour in the flask changes to red. With acid the following reactions take place :

$$Ca(HCO_3)_2+H_2SO_4 \longrightarrow CaSO_4+CO_2+H_3O$$

$$Mg(HCO_3)_2+H_2SO_4 \longrightarrow MgSO_4+CO_2+H_2O$$

At this stage boil the solution to drive off the CO_2 from the solution (produced as a result of decomposition of carbonates and bicarbonates). You will notice that the red colour disappears while the solution is being boiled. Now add more of the acid from the burette to boiling solution until the red colour is permanent. Note the amount of total acid required in titration.

B. Estimation of permanent hardness

Take 100 mL of hard water in a clean porcelain dish. Add 12.5 mL of 0.1 N sodium carbonate solution to precipitate calcium as calcium carbonate. Also add 12.5 mL of 0.1 N sodium hydroxide to precipitate magnesium as magnesium hydroxide.

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$$
$$MgSO_4 + 2NaOH \longrightarrow Mg(OH)_2 + Na_2SO_4$$

Heat the dish on a water bath until the water is evaporated and a solid mass is left behind.

Treat the residue with freshly boiled distilled water (free from CO_2) and shake.

Filter through a filter paper and wash the residue with more of boiled distilled water. Collect the filtrate.

Titrate the filtrate with 0.1 N sulphuric acid using methyl red indicator.

Repeat the procedure with 100 mL of distilled water for blank reading.

Observations :

A. Volume of 0.02 N sulphuric acid used for 100 mL water =X mL

B. (1) Volume of 0.1 N sulphuric acid used by 100 mL of sample water=Y mL

(2) Volume of 0.1 N sulphuric acid used in blank determination=Z mL

(3) Volume of 0.1 N sulphuric acid actually used for 100 mL of sample water=(Y−Z) mL

Calculations :

Part A

1 mL of 0.02 N sulphuric acid ≡ 10 parts of calcium carbonate per million

X mL of 0.02 N sulphuric acid = 10 X p.p.m. of calcium carbonate

Part B

1 mL of 0.1 N sulphuric acid = 50 p.p.m. of $CaCO_3$

(Y—Z) mL of 0.1 N sulphuric acid = (Y—Z) 50 p.p.m. of calcium carbonate

Total hardness of water = 10 X + (Y—Z) 50 p.p.m. of calcium carbonate

Result :

The total hardness of a given sample of water is......p.p.m. of calcium carbonate.

QUESTIONS

1. What is meant by hard water and its hardness ?
2. Suggest methods to remove hardness of water.
3. What is soap ? How does it differ from detergent ?
4. It is healthier to take hard water. Comment.
5. What are the disadvantages of hard water in industries ?

14.6. CHEMICAL SANITIZERS

Chemical sanitizers find their uses in **sanitization**, a process of reducing microbial load of the surfare to be sanitized. For this purpose, apart from chemicals, application of heat and ultraviolet radiations has also been effective. Sodium hypochlorite and bleaching powder are widely used for sanitization. Both these compounds contain chlorine which serve the purpose. These compounds on reacting with dilute acids (e.g. H_2SO_4) give whole of chlorine which is known as **available chlorine**.

$$2NaOCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HOCl$$

$$2HOCl \rightleftharpoons H_2O + Cl_2 + \tfrac{1}{2}O_2$$

$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$$

Experiment 14.6.1. To determine the available chlorine in chlorine containing sterilizers.

General : It is necessary to check the amount of available chlorine in the sterilizer to determine the strength of the chemical. It is done by the reaction between hypochlorite solution and acidified potassium iodide.

Apparatus : Conical flask 250 mL, burette, pipettes, measuring cylinder.

Chemicals : Glacial acetic acid, potassium iodide, sodium thiosulphate solution 0.1 N, starch solution, 1%, sodium hypochlorite solution.

$$NaOCl + 2KI + 2CH_3COOH \longrightarrow NaCl + 2CH_3COOK + I_2 + H_2$$

The liberated iodine is then titrated against 0.1 N sodium thiosulphate ($Na_2S_2O_3.5H_2O$)

$$I_2+2Na_2S_2O_3 \longrightarrow Na_2S_4O_6+2NaI$$

One molecule of sodium thiosulphate is equivalent to one atom of iodine or one atom of chlorine. Its molecular mass is 248.2 and its 0.1 N solution contains 24.82 g per litre. It follows that every mL of 0.1 N solution is equivalent to 0.003546 g available chlorine.

Procedure : Take the sodium hypochlorite solution sample available in the market. Pipette out 5 mL of the sample solution into a 250 mL volumetric flask and dilute with distilled water to make the volume upto mark. Shake the solution well.

Pipette out 50 mL of dilute solution into a conical flask. Add 2g of potassium iodide crystals to the solution and dissolve them. Now add 10 mL of glacical acetic acid.

As a result of reaction between NaCl and acid, free chlorine is liberated which in turn reacts with KI present in the solution. Iodine is evolved which imparts light brownish yellow colour to the solution.

Titrate the reaction mixture against 0.1 N sodium thiosulphate until the brown colour changes to light straw yellow.

At this stage add 2 mL of one per cent starch solution as indicator. Continue titration by addition of thiosulphate solution drop by drop until the colour disappears.

Repeat the experiment to get concordant values.

Observations and Calculations

Record the titre values in the tabular form.

Strength of sodium thiosulphate $=f\times 0.1$ N

Volume of 0.1 N sodium thiosulphate $=v$ mL required

1 mL of 0.1 N sodium thiosulphate $\equiv$ 0.003546 g available chlorine

1 mL of $f\times 0.1$ N sodium thiosulphate $=f\times 0.003546$ g available chlorine (f=factor)

V mL of $f\times 0.1$ N sodium thiosulphate $=v\times f\times 0.003546$ g available chlorine

This was contained in 50 mL of diluted solution or 1 mL of the original sample.

Therefore available chlorine in 100 mL of the sample solution of NaOCl

$=v\times f\times 0.003546\times 100$ g

or $=v\times f\times 0.3546$ per cent.

QUESTIONS

1. What is meant by 'available chlorine' ?

2. Aqueous solution of sodium hypochlorite appears yellowish green. Comment.

3. Commercial bleaching powder contains 35% available chlorine. Comment.

4. Suggest methods for the preparation of sodium hypochlorite and bleaching powder.

5. Distinguish between the bleaching action of sulphur dioxide and chlorine.

Now I am sure students can plan investigatory projects of their taste after discussing from their class teachers.

Some projects are suggested below for your reference :

1. Study of diffusion of a solid into a liquid.
2. Determination of the minimum quantity of manganese dioxide required as a catalyst for the preparation of oxygen gas.
3. Determination of rate of flow of solutions and liquids horizontally.
4. Investigation on the foaming capacity of different washing soaps and the effect of addition of sodium carbonate on them.
5. Study of the acidity of different samples of the tea leaves and reasons for the variation in their taste.
6. Determination of the rate of evaporation of different liquids.
7. Study of the effect of *metal coupling* on the corrosion of iron.
8. Study of the effect of acids and bases on the tensile strength of fibres.
9. Analysis of fruit and vegetable juices for the contents (acids and minerals) present in them.
10. Preparation of rayon threads from various cellulose sources.
11. Study of dyeing of fabrics under various conditions.
12. Determination of the dosage of bleaching powder required for disinfection of different samples of water (taken from different sources).
13. Study of the presence of oxalate ions in guava fruit at different stages of ripening.
14. Study of the setting of mixtures of cement with lime, sand of different qualities, rice husk, etc. (with respect to time, volume and strength).
15. Study of the presence of insecticide/pesticide (nitrogen containing) in vegetables and fruits.

16. Study of the dialysis of different sewage water samples and identification of different ions in resulting solutions.
17. Study of the quantity of case in present in different samples of milk.
18. Preparation of Soyabean milk and its comparison with the natural milk with respect to curd formation, effect of temperature, taste, etc.
19. Study of the effect of potassium bisulphate as food preservative under various conditions (temperature, concentration, time, etc.).
20. Study of digestion of starch by salivary amylase and effect of *p*H and temperature on it.
21. Comparative study of the rate of formation of following substances, wheat flour, gram flour, potato juice, carrot juice and organic juice.
22. Extraction of essential oils present in Saunf (Aniseed), Ajwain (Carum), Illachi (cardamom).
23. Study of constituents of an alloy (any sample easily available may be taken).
24. Study of common food adulterants in fat, oil, butter, sugar, turmeric powder, chilli powder and pepper.

Note : Any other investigatory project can be performed which involves about 10 periods of work with the approval of the teacher.

□ □

Appendix

Preparation of reagent solutions :

Reagent	*Approximate normality*	*Preparation of 1 litre solution*
Ammonium acetate	3 N	Dissolve 231 g in water and dilute to volume.
Ammonium carbonate	4 N	Dissolve 160 g in a mixture of 140 mL of conc. ammonia and 860 mL of water.
Ammonium chloride	5 N	Dissolve 270 g in water and dilute it to volume.
Ammonium nitrate	1 N	Dissolve 80 g in water and dilute it to volume.
Ammonium oxalate	0.5 N	Dissolve 34 g in water and dilute it to volume.
Ammonium sulphate	2 N	Dissolve 132 g in water and dilute it to volume.
Ammonium sulphide (yellow)	6 N	Pass H_2S gas through 150 mL of concentrated ammonia solution in cold until it is saturated ; add 10 g of flowers of sulphur and 250 mL of conc. ammonia solution. Shake the mixture until the sulphur is dissolved and finally dilute with distilled water to volume.
Barium chloride	0.5 N	Dissolve 61 g in water and dilute it to volume.
Calcuim chloride	0.5 N	Dissolve 55 g in water and dilute it to volume.
Cobalt nitrate	0.3 N	Dissolve 44 g in water and dilute it to volume.
Copper sulphate	0.5 N	Dissolve 125 g in about 500 mL water containing 3 mL of conc. H_2SO_4. Make up the volume.
Ferric chloride	0.5 N	Dissolve 135 g in about 500 mL of water containing 20 mL of conc. HCl Make up the volume.
Iodine solution	0.1 N	Dissolve 12.7 g iodine in a solution containing 20 g of KL in 30 mL of water and finally dilute with water to volume.

Reagent	*Approximate normality*	*Preparation of 1 litre solution*
Lead acetate	0.5 N	Dissolve 95 g in water containing conc. HCl and dilute it to volume.
Mercuric chloride	0.2 N	Dissolve 27 g in water and dilute it to volume.
Potassium chromate	0.5 N	Dissolve 49 g in water and dilute it to volume.
Potassium ferri-cyanide	0.5 N	Dissolve 32.5 g in water and dilute it to volume.
Potassium ferro-cyanide	0.5 N	Dissolve 53 g in water and dilute it to volume.
Potassium iodide	0.5 N	Dissolve 83 g in water and dilute it to volume.
Potassium permanganate	0.1 N	Dissolve 3.2 g in water, dilute to volume and finally filter through glass wool.
Potassium thiocyanate	0.5 N	Dissolve 49 g in water and dilute it to volume.
Silver nitrate	0.1 N	Dissolve 17 g in water and dilute it to volume. Store in a coloured bottle.
Sodium hydrogen phosphate	1 N	Dissolve 120 g in water and dilute it to volume.
Stannous chloride	0·5 N	Dissolve 56 g in 100 mL of conc. HCl and then dilute with water to 1 litre. Add a few pieces of tin metal.
Neutral $FeCl_3$ solution		Add NaOH solution drop by drop to $FeCl_3$ solution until a slight ppt. persists on shaking. Now add dil. HCl in drops until the ppt. just dissolves.
Nessler's reagent		Dissolve 23 g of mercuric iodide and 16 g of KI in distilled water (free of NH_3) and dilute to 100 mL. Then add 100 mL of 6N-NaOH solution.

Solid Reagents. Aluminium powder, Ammonium chloride, Borax, Calcium chloride, Lead dioxide, Magnesium metal, Potassium nitrite, Potassium permanganate, Potassium bisulphate, Potassium dichromate, Potassium iodide, Sodium nitrate, Sodium bicarbonate, Sodium nitrite, Sodium peroxide, Sodium bisulphate, Zinc metal, Zinc chloride, α-naphthol.

Indicators

Phenolphthalein solution. Dissolve 5 g of phenolphthalein in 50 mL of rectified spirit and 500 mL water with constant stirring. Filter, if necessary.

Litmus solution (blue). Dissolve 10 g of the solid in 100 mL of water.

Litmus solution (red). To 1% blue litmus soln. prepared above, add a few drops of HCl until the solution acquires a red colour.

Methyl orange solution. Dissolve 1 g of solid in one litre of hot water and filter.

Methyl red solution. Dissolve 1 g of solid in 0.5 litre of alcohol and dilute with water to one litre.

Reagents for Organic Analysis

Reagent	*Preparation of reagent solution*
Alcoholic silver nitrate	Prepare 10% solution of $AgNO_3$ in alcohol.
Barford's reagent	Dissolve 6.5 g of copper acetate crystals in 100 mL of 1% acetic acid.
Benedict's solution	Dissolve 1.73 g of crystals of copper sulphate in 100 mL of water and add 17.3 g of sodium citrate and 10 g of anhydrous Na_2CO_3 in 80 mL of water. Dilute the solution to 500 mL with water.
2 : 4 Dinitrophenylhydrazine	Dissolve 2 g of reagent in 10 mL of conc. H_2SO_4. Then slowly add 200 mL of alcohol. Filter after sometime.
Fehling's solution	Dissolve 34.5 of copper sulphate in 500 mL of water. Add a few drops of H_2SO_4 (if necessary) to make the solution clear. (Fehling's solution A). Dissolve 173 g of Rochelle salt (sodium potassium tartarate) and 50 g of NaOH in water and dilute to 500 mL (Fehling's solution B). Mix solutions A and B in equal volumes, whenever required.
Molisch's reagent	Dissolve 10 g of α-naphthol in 100 mL of rectified spirit.
Schiff's reagent	Pass SO_2 gas through 1% solution of Fuschine (rosanaline) until its colour is discharged. Filter and store the solution in a coloured stoppered bottle.
Tollen's reagent	Mix 2 mL of 10% NaOH with 2 mL of 10% $AgNO_3$ solution. Then add aqueous ammonia solution dropwise until the solution is colourless.
Millon's reagent	Dissolve 10 g of mercury in 20 mL of hot concentrated nitric acid and dilute the resulting solution with 30 mL water.
Huble's reagent	Dissolve mercuric chloride in iodine solution (iodine solution is prepared by dissolving iodine in potassium iodide).

International Atomic Masses

Element	*Symbol*	*Atomic number*	*Atomic mass* (amu)
Aluminium	Al	13	26.9815
Antimony	Sb	51	121.75
Arsenic	As	33	74.9216
Barium	Ba	56	137.34
Bismuth	Bi	83	208.280
Boron	B	5	10.811
Bromine	Br	35	79.909
Cadmium	Cd	48	112.40
Calcium	Ca	20	40.08
Carbon	C	6	12.01115
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.996
Cobalt	Co	27	58.9332
Copper	Cu	29	63.54
Fluorine	F	9	18.9984
Gold	Au	79	196.967
Hydrogen	H	1	1.00797
Iodine	I	53	126.9043
Iron	Fe	26	55.847
Lead	Pb	82	207.19
Lithium	Li	3	6.939
Magnesium	Mg	12	24.312
Manganese	Mn	25	54.9380
Mercury	Hg	80	200.59
Nickel	Ni	28	58.71
Nitrogen	N	7	14.0067
Oxygen	O	8	15.9994
Phosphorus	P	15	30.9738
Platinum	Pt	78	195.09
Potassium	K	19	39.102
Silicon	Si	14	28.086
Silver	Ag	47	107.870
Sodium	Na	11	22.9898
Strontium	Sr	38	87.62
Sulphur	S	16	32.064
Tin	Sn	50	118.69
Uranium	U	92	238.03
Zinc	Zn	30	65.37

[**Note.** Values are based on the C—12 standard].

APPENDIX

Logarithm Tables

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170						5	9	13	17	21	26	30	34	38
						0212	0253	0294	0334	0374	4	8	12	16	20	24	28	32	36
11	0414	0453	0492	0531	0569						4	8	12	16	20	23	27	31	35
						0607	0645	0682	0719	0755	4	7	11	15	18	22	26	29	33
12	0792	0828	0864	0899	0934						3	7	11	14	18	21	25	28	32
						0969	1004	1038	1072	1106	3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271						3	6	10	13	16	19	23	26	29
						1303	1335	1367	1399	1430	3	7	10	13	16	19	22	25	29
14	1461	1492	1523	1553	1584						3	6	9	12	15	19	22	25	28
						1614	1644	1673	1703	1732	3	6	9	12	14	17	20	23	26
15	1761	1790	1818	1847	1875						3	6	9	11	14	17	20	23	26
						1903	1931	1959	1987	2014	3	6	8	11	14	17	19	22	25
16	2041	2068	2095	2122	2148						3	6	8	11	14	16	19	22	24
						2175	2201	2227	2253	2279	3	5	8	10	13	16	18	21	23
17	2304	2330	2355	2380	2405						3	5	8	10	13	15	18	20	23
						2430	2455	2480	2504	2529	3	5	8	10	12	15	17	20	22
18	2553	2577	2601	2625	2648						2	5	7	9	12	14	17	19	21
						2672	2695	2718	2742	2765	2	4	7	9	11	14	16	18	21
19	2788	2810	2833	2856	2878						2	4	7	9	11	13	16	18	20
						2900	2923	2945	2967	2989	2	4	6	8	11	13	15	17	19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4083	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	123	456	789
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1 2 3	3 4 5	6 7 8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1 2 3	3 4 5	6 7 8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1 2 2	3 4 5	6 7 7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1 2 2	3 4 5	6 6 7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1 2 2	3 4 5	6 6 7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1 2 2	3 4 5	5 6 7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1 2 2	3 4 5	5 6 7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1 2 2	3 4 5	5 6 7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1 2 2	3 4 5	5 6 7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1 1 2	3 4 4	5 6 7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1 1 2	3 4 4	5 6 6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1 1 2	3 4 4	5 6 6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1 1 2	3 4 4	5 6 6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1 1 2	3 3 4	5 6 6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1 1 2	3 3 4	5 5 6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1 1 2	3 3 4	5 5 6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1 1 2	3 3 4	5 5 6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1 1 2	3 3 4	5 5 6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1 1 2	3 3 4	5 5 6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1 1 2	2 3 4	4 5 6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1 1 2	2 3 4	4 5 6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1 1 2	2 3 4	4 5 5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1 1 2	2 3 4	4 5 5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1 1 2	2 3 4	4 5 5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1 1 2	2 3 4	4 5 5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1 1 2	2 3 3	4 5 5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1 1 2	2 3 3	4 5 5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1 1 2	2 3 3	4 4 5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1 1 2	2 3 3	4 4 5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1 1 2	2 3 3	4 4 5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1 1 2	2 3 3	4 4 5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1 1 2	2 3 3	4 4 5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1 1 2	2 3 3	4 4 5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1 1 2	2 3 3	4 4 5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1 1 2	2 3 3	4 4 5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1 1 2	2 3 3	4 4 5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1 1 2	2 3 3	4 4 5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0 1 1	2 2 3	3 4 4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0 1 1	2 2 3	3 4 4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0 1 1	2 2 3	3 4 4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0 1 1	2 2 3	3 4 4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0 1 1	2 2 3	3 4 4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0 1 1	2 2 3	3 4 4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0 1 1	2 2 3	3 4 4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0 1 1	2 2 3	3 4 4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0 1 1	2 2 3	3 4 4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0 1 1	2 2 3	3 4 4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0 1 1	2 2 3	3 4 4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0 1 1	2 2 3	3 4 4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0 1 1	2 2 3	3 3 4

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	123	456	789
·00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0 0 1	1 1 1	2 2 2
·01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0 0 1	1 1 1	2 2 2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0 0 1	1 1 1	2 2 2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0 0 1	1 1 1	2 2 2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0 1 1	1 1 2	2 2 2
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0 1 1	1 1 2	2 2 2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0 1 1	1 1 2	2 2 2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0 1 1	1 1 2	2 2 2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0 1 1	1 1 2	2 2 3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0 1 1	1 1 2	2 2 3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0 1 1	1 1 2	2 2 3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0 1 1	1 2 2	2 2 3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0 1 1	1 2 2	2 2 3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0 1 1	1 2 2	2 3 3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0 1 1	1 2 2	2 3 3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0 1 1	1 2 2	2 3 3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0 1 1	1 2 2	2 3 3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0 1 1	1 2 2	2 3 3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0 1 1	1 2 2	2 3 3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0 1 1	1 2 2	3 3 3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0 1 1	1 2 2	3 3 3
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0 1 1	2 2 2	3 3 3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0 1 1	2 2 2	3 3 3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0 1 1	2 2 2	3 3 4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0 1 1	2 2 2	3 3 4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0 1 1	2 2 2	3 3 4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0 1 1	2 2 3	3 3 4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0 1 1	2 2 3	3 3 4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0 1 1	2 2 3	3 4 4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0 1 1	2 2 3	3 4 4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0 1 1	2 2 3	3 4 4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0 1 1	2 2 3	3 4 4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0 1 1	2 2 3	3 4 4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0 1 1	2 2 3	3 4 4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1 1 2	2 3 3	4 4 5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1 1 2	2 3 3	4 4 5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1 1 2	2 3 3	4 4 5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1 1 2	2 3 3	4 4 5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1 1 2	2 3 3	4 4 5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1 1 2	2 3 3	4 5 5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1 1 2	2 3 4	4 5 5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1 1 2	2 3 4	4 5 5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1 1 2	2 3 4	4 5 6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1 1 2	3 3 4	4 5 6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1 1 2	3 3 4	4 5 6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1 1 2	3 3 4	5 5 6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1 1 2	3 3 4	5 5 6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1 1 2	3 3 4	5 5 6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1 1 2	3 4 4	5 6 6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1 1 2	3 4 4	5 6 6

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
·52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
·55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
·56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
·57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
·58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
·59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
·60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	[illegible]	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	[illegible]

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